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AQUEOUS VAPOR PRESSURE OF SOILS: II. STUDIES IN DRY SOILS

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HISTORICAL

An earlier paper (18) described the vapor pressure as a function of the moisture content, with special reference to comparatively moist soils. The present study is concerned with this function in drier soils, as it is influenced by their chemical composition, size distribution, and previous treatment.

The vapor-pressure moisture relations of soils have been studied to some extent by several investigators, all of whom used the method of allowing small samples to stand in desiccators containing sulfuric acid of known strength and vapor pressure until equilibrium was established after which the moisture content of the soil was determined. If vapor pressure is plotted as ordinate and moisture content as abscissa there is fairly good agreement in the shape of all the published curves. The coarser the texture of the soil the nearer the curves lie to the axis of ordinates. Their upper portions are concave downward, indicating the hyperbolic form already described (18, p. 421). At intermediate pressures they are nearly straight lines, the slope decreasing as the texture becomes finer, while at very low pressures they sometimes show a sharp inflexion as they approach the origin and are concave upward (8). The curves appear to be free from discontinuity such as might be caused by chemical hydrates. Van Bemmelen (19) found this to be true also of the vapor-pressure curves of colloidal silica, alumina, and ferric oxide.

It has been supposed that at a given vapor pressure the moisture is held on the surface of the soil grains by a definite force of attraction which corresponds to definite thickness of water film. It is only necessary, therefore, to determine the moisture content of a soil in equilibrium with an atmosphere of a certain arbitrarily chosen relative humidity in order to arrive at a value which, if it is not directly proportional to the total soil surface, is at least a very useful index of texture. The "hygroscopic coefficient" of Hilgard (10) and Alway (2) and the "hygroscopicity" of Rodewald and Mitscherlich (17) are based on this idea. The latter go so far as to assume, from a study of the heat of wetting, that the moisture absorbed by standing over 10 per cent sulfuric acid is distributed as a mono-molecular film over the soil surface, which they proceed to estimate from a knowledge of the size of a water molecule. Their results have been discredited by Odén (15) and Ehrenberg (7) as being too large and of doubtful significance for comparative purposes if appreciable amounts of colloidal material are present.

An obvious way to test this hypothesis quantitatively is to determine the total surface of the soil from the mechanical analysis and calculate the thickness of the water film. The data on this point in the literature are conflicting. Briggs (4) estimated the thickness of the water film on powdered quartz in an atmosphere of 99 per cent humidity to be 4.5×10^{-6} mm. Patten and Gallagher (16) found the value 3×10^{-4} mm. for soil separate 0.1–0.05 mm. in diameter in a saturated atmosphere. They also obtained results of the same order of magnitude for a number of soils and quote Parks as having given the value, 1.34×10^{-4} mm.,

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for glass wool. Odén (14) found that the amount of water per unit of surface at a given vapor pressure varied over a considerable range in different soils and was only constant when the soils compared were nearly identical. The thickness of the water film in a saturated atmosphere was about 2×10^{-5} to 3×10^{-5} mm., whereas at a very low vapor pressure where the curves were inflected toward the origin the thickness was of the order of 10^{-6} mm.

Langmuir's (13) work would indicate that the range of molecular attraction is less than the distance across an ordinary molecule and that therefore a truly absorbed film is never more than one or two molecules thick. The apparent thickness of the films noted above is due to the porous nature of the absorbing surfaces which hold part of the water by capillarity. Harkins and his coworkers (9) have developed a general thermo-dynamic criterion of film formation called the "coefficient of spreading," based on the surface tensions of the absorbing and absorbed substances and their interfacial tension. According to the numerical value of this "coefficient" a film may not form at all or its thickness may range from mono-molecular dimensions up to a micron, though thick films are probably rare. Unfortunately, the application of this criterion at present is precluded by the lack of surface tension data for solids.

The Bureau of Soils (1) has recently proposed absorption of water over 2 per cent sulfuric acid as a method of estimating the amount of "colloidal" material in soil.

TABLE 1

Description of the natural Utah soils

LABORA-TORY NUMBER	TYPE NAME	CLASS	SOURCE	DEPTH OF SAMPLE	STRUCTURE	SOLUBLE SALTS
			County			*per cent*
T1	Trenton	Clay	Cache	Subsoil		0.126
G1*	Millville	Silty clay loam	Cache	Surface soil		0.038
WL.†	Millville	Clay loam	Cache	Surface soil		0.130
B5		Sandy loam	Davis	Surface soil		
168‡	Naples	Clay loam	Uinta	0–⅛ in.	Crust	0.050
169‡	Naples	Clay loam	Uinta	⅛–1 in.	Plate structure	0.060
170‡	Naples	Clay	Uinta	1–6 in.	Pea structure	0.060
172‡	Naples	Clay	Uinta	9–15 in.	Compact layer	0.100
507‡	Abbott	Clay	Millard	0–⅛ in.	Crust	0.120
508‡	Abbott	Clay	Millard	⅛–4 in.	Compact layer	.....
629‡	Bennett	Sandy loam	Uinta	⅛– 2 in.	Mulch	.....
631‡	Bennett	Sandy clay	Uinta	18–24 in.	Compact layer	.....
993‡	Cache	Clay	Cache	0–4 in.		1.520
994‡	Cache	Clay	Cache	4–10 in.		1.580

* From Greenville Farm.

† From West Logan.

‡ Part of virgin profile.

DESCRIPTION OF THE SOILS

Source

The vapor-pressure moisture relations reported below were investigated in three stages:

(1) A group of chemically similar soil separates ranging from fine sands to tight clays was first studied. These soils form a part of a series prepared by W. Gardner of this station from Trenton clay by elutriation. They are numbered S5–S19 to indicate their order of preparation, the larger numbers representing finer textures. In preparing them it was

TABLE 2

Chemical analysis of the soils (dried at 110°C.)

	SOIL S7	SOIL SW7	SOIL S13	SOIL S15	SOIL S18	SOIL TRENTON	SOIL T7	SOIL G1	SOIL W.L.	SOIL 168	SOIL 169	SOIL 170	SOIL 172	SOIL 508	SOIL 629	SOIL 631	SOIL 994	SOIL B5
	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent
SiO_2	44.28	43.40	43.94	43.50	42.23	40.10	51.25	39.40	49.70	67.62	65.21	60.26	61.26	49.12	90.02	81.05	50.50	64.90
CO_2	21.20	22.72	16.38	15.50	15.30	15.63	2.36	18.30	14.40	4.68	4.90	5.58	6.26	8.66	0.14	0.45	8.85	0.00
Al_2O_3	4.42	2.40	8.57	9.75	10.72	9.79	18.52	7.65	7.14	8.98	9.60	11.19	9.73	12.24	2.99	7.71	11.31	11.51
Fe_2O_3	1.31	1.50	3.20	3.86	3.90	3.88	6.56	3.26	2.65	2.70	3.43	3.60	3.31	5.30	1.72	3.27	3.65	6.47
CaO	16.18	17.10	15.41	14.90	15.71	17.80	3.71	13.46	12.60	5.90	6.33	7.81	7.98	10.34	0.45	1.21	11.35	2.83
MgO	9.24	9.80	6.70	6.13	5.46	5.05	5.48	9.90	6.55	2.55	2.80	3.14	3.26	4.92	0.86	1.35	3.82	2.34
Na_2O	0.47	0.56	0.56	0.42	0.42	0.52	0.20	0.51	0.66	0.80	0.84	0.82	0.83	0.26	0.66	0.68	1.62	1.63
K_2O	1.36	1.50	1.89	1.97	2.29	2.50	3.77	2.25	1.76	2.30	2.60	2.72	2.45	2.64	1.06	1.48	2.31	2.29
H_2O	0.81	0.53	2.37	2.88	3.33	3.52	6.90	3.22	2.46	2.82	3.30	4.26	3.30	5.50	1.25	2.32	4.33	4.21
TiO_2	0.34	0.37	0.48	0.50	0.51	0.47	0.62	0.46	0.46	0.69	0.61	0.58	0.74	0.62	0.34	0.53	0.63	1.01
P_2O_5	0.17	0.17	0.19	0.20	0.23	0.20	0.20	0.25	0.29	0.18	0.26	0.23	0.225	0.24	0.25	0.09	0.36	0.26
SO_3	0.04	*	0.05	0.052	0.088	0.05	*	0.031	0.05	0.002	0.004	0.004	0.012	*	*	*	0.03	*
Cl	*	*	*	*	*	0.02	*	0.008	Trace	0.00	0.00	0.00	0.00	*	*	*	1.08	*
CrO_2						0.005		0.005	0.005									
MnO	0.025	†	0.041	0.052	0.06	0.06	†	0.07	0.056	†	†	†	†	†		†	†	†
SrO	*					Trace	†	Trace	Trace	†	†	†	†	†		†	†	†
BaO	*	*	*	*	*	0.04	*	0.036	0.036	*	*	*	*	*	*	*	*	*
N	*	*	0.036	0.036	0.05	0.075	*	0.14	0.10	0.07	0.044	0.035	0.033	0.079	0.035	0.055	0.05	0.10
C	0.25	0.11	0.44	0.40	0.20	0.68	0.33	1.62	1.32	0.41	0.22	0.29	0.36	0.75	0.33	0.53	0.49	2.55
Total	100.10	100.16	100.26	100.15	100.50	100.39	99.90	100.57	100.24	99.70	100.15	100.52	99.75	100.67	100.10	100.72	100.47	100.10

* Not determined.

† Present, but not determined quantitatively.

hoped to obtain material having only a small range of size of particles, but the failure to use deflocculating agents in the elutriator defeated this hope. Nevertheless, they offer a good opportunity to study the influence of texture on vapor pressure when the chemical composition is approximately constant.

(2) The Trenton clay was next considered after subjecting it to a number of wetting and drying treatments.

(3) Finally the inquiry was carried to a group of nineteen other natural and artificial soils representing a wide range of texture, mechanical distribution, and chemical composition. The natural soils were supplied by D. S. Jennings of this station. They are described in table 1. The artificial soils were true separates numbered S.W.5–S.W.9 and were made from the corresponding soils of Gardner's series by shaking them for several hours with 1 per cent sodium carbonate and subsequently decanting. This process was repeated many times to remove the colloidal content. Soils T5, T6, and T7 were prepared from Trenton clay by sedimentation. Soil T5 was free from removable colloid and had sharp limits of size between 0.5 and 1.5 micron radius. When dried it formed a soft cake which could be easily disintegrated to a fluffy white powder. Soils T6 and T7 were highly colloidal. When dried they formed hard, polished horn-like cakes. Soil T6 was brownish gray in color, while T7 was dark brown.

Chemical composition

Complete chemical analyses of all the soil types are given in table 2. The soils range from highly calcareous to highly silicious materials. They are generally low in organic matter although three contain moderate amounts. Gardner's separates show an increase in the iron, alumina, potassium, and water and a decrease in the silica, magnesium, and carbonate carbon as the texture becomes finer, but the differences are slight. These changes are very marked in soil T7, but the low value of the carbonate is probably due in part to the fact that in its preparation the colloidal suspension was coagulated by carbon dioxide which dissolved part of the lime. The range of the carbonate content in the other soils is noteworthy. It should be pointed out that the two Cache soils differ noticeably in the respect and that soil 993 contained only 0.96 per cent carbon dioxide.

Mechanical composition

Complete mechanical analyses of all the soils have been made by the method recently developed at this station (11). The data are given graphically in figure 1 in which the ordinate shows the percentage of material of smaller radius than the value of the corresponding abscissa. The curves appear to extrapolate to the zero ordinate at about 0.01 micron radius, and this extrapolation has been made use of in calculating the total surfaces of the soils. Gardner's separates are shown in chart A. They fall in the expected order. Soil 631 is particularly interesting because it is almost entirely lacking in silt.

In carrying out the analyses every effort was made to secure complete dispersion. Two hours of shaking with 0.5 per cent sodium carbonate was not sufficient to deflocculate a sample of heavy soil which had been oven-dried or thoroughly air-dried. This is indicated in the insert in chart C, figure 1, which shows the result of these treatments on Trenton clay. It seems evident, therefore, that drying a soil makes its texture coarser, in effect, by dehydrating the colloids and making them adhere more firmly to the larger particles. Prolonged shaking or contact with water will reverse this condition. In the analyses reported in this paper the samples were allowed to stand moist for several weeks, after which they were shaken for eight to fifteen hours with 0.5 per cent sodium carbonate. If the soil contained an appreciable amount of soluble salt this was removed by decantation before shaking.

Fig. 1. Mechanical Composition of the Soils
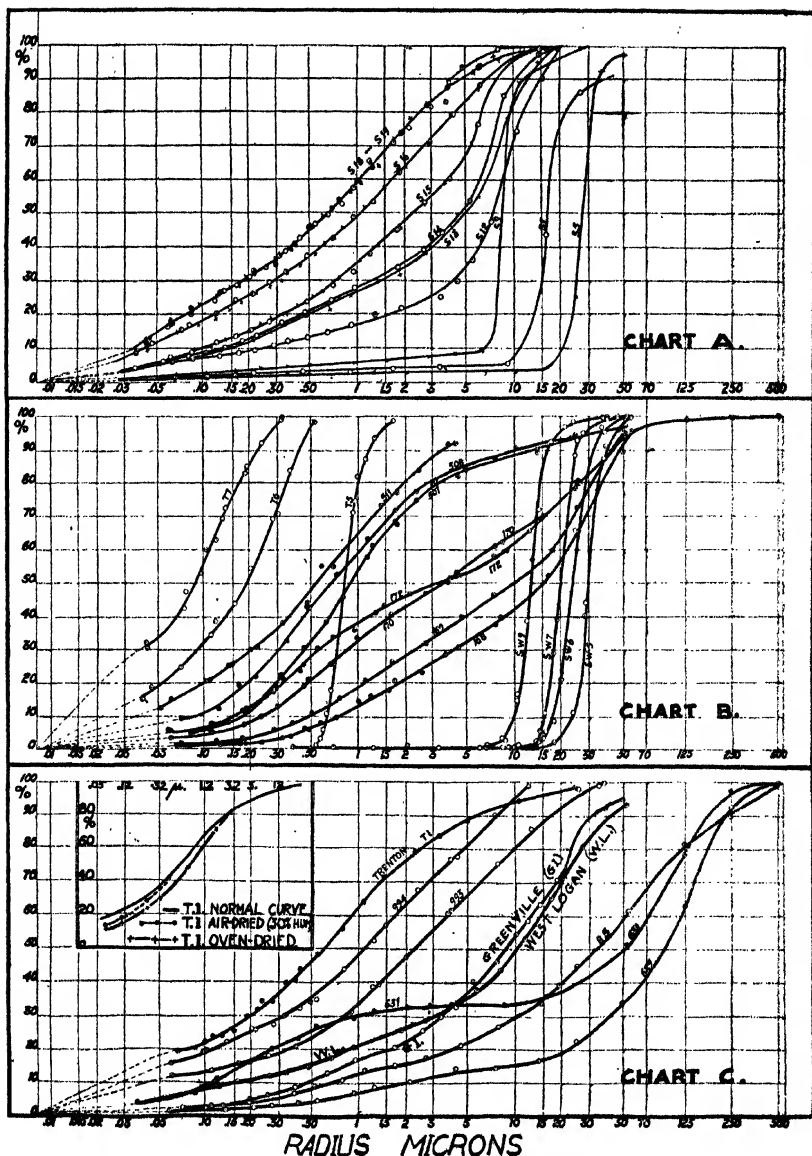
The ordinate represents the percentage of material of smaller radius than the value of the corresponding abscissa. The insert in Chart C illustrates the effect of drying treatment on the mechanical analysis.

TECHNIQUE

Both the static and dynamic methods have been used in this work to measure the vapor pressure of the soil. The static method consists in exposing 5-to 10-gram samples of soil in small aluminum cans, provided with close-fitting covers, over sulfuric acid of known strength in a well exhausted vacuum desiccator until equilibrium is established. The moisture content of the soil is then determined. Twenty to thirty cans may be placed in an 8-inch desiccator which is stored in an insulated box in a deep basement room to prevent appreciable fluctuations of temperature. Moisture determinations are made by drying the soil in a large electric oven at 110° for forty-eight hours. The most important considerations for accuracy in this operation are to cover the cans quickly after opening the oven and to cool them in a good desiccator containing phosphorus pentoxide.

The apparatus for the dynamic method is the same as that already described, except that the presaturator is enlarged. It has been found expedient, however, in dealing with dry soils whose vapor pressure are much lower than that of water to adopt the Washburn (20) arrangement of the experiment:

A slow current of air is passed through the presaturator containing a sulfuric acid solution about the same vapor pressure as that of the soil, then through the soil sample contained in large brass tubes, and finally through a weighed moisture absorber. The dry air is now completely saturated with water vapor by passing it through a series of horizontal tubes partly filled with water and dried again in another absorber. The whole apparatus is immersed in a well controlled thermostat at 25°C. From the increase in weight of the two absorbers the vapor pressure of the soil may be calculated. The preliminary adjustment of the water-vapor content of the air is necessary in order to avoid a change in the moisture content of the soil.

In practice, the same air may be passed through two or more sets of soil tubes before being finally saturated in the water vessel. The pressure in each section of the apparatus is read on oil manometers. In this way several vapor-pressure measurements may be made at one time.

The static method is less laborious, operates on a smaller soil sample, and, provided enough cans and desiccators are available, permits the carrying out of a large number of determinations at one time. Though it may require several weeks or even months for equilibrium to be established in a given experiment, the apparatus needs no attention during this time. The two methods give closely agreeing results with dry and moderately moist soils, but it is doubtful if the static process is sufficiently accurate or rapid to be used in studying moist soils.

EXPERIMENTAL RESULTS

Gardner's separates

The dynamic method was employed in carrying out the experiments with the separates. The dry soils were uniformly wetted by successive small amounts of liquid water, as already described (18, p. 415). After each wetting, the soil samples stood closed in a bottle with occasional shaking for three to seven days before vapor-pressure measurements were made. When complete curves were thus obtained the soils were dried in the air and the whole process was repeated. The data are given in figure 2, chart A, in which the abscissae represent the moisture percentage and the ordinates the vapor pressure in per cent of the vapor pressure of water. Each point is the mean of two or more closely agreeing duplicate determinations. The order of the curves is qualitatively in agreement with the order of the separates. The curves for the soils S13 to S19, inclusive, are shifted very materially to the right as a result of wetting and subsequently air-drying. This is due to the fact that these
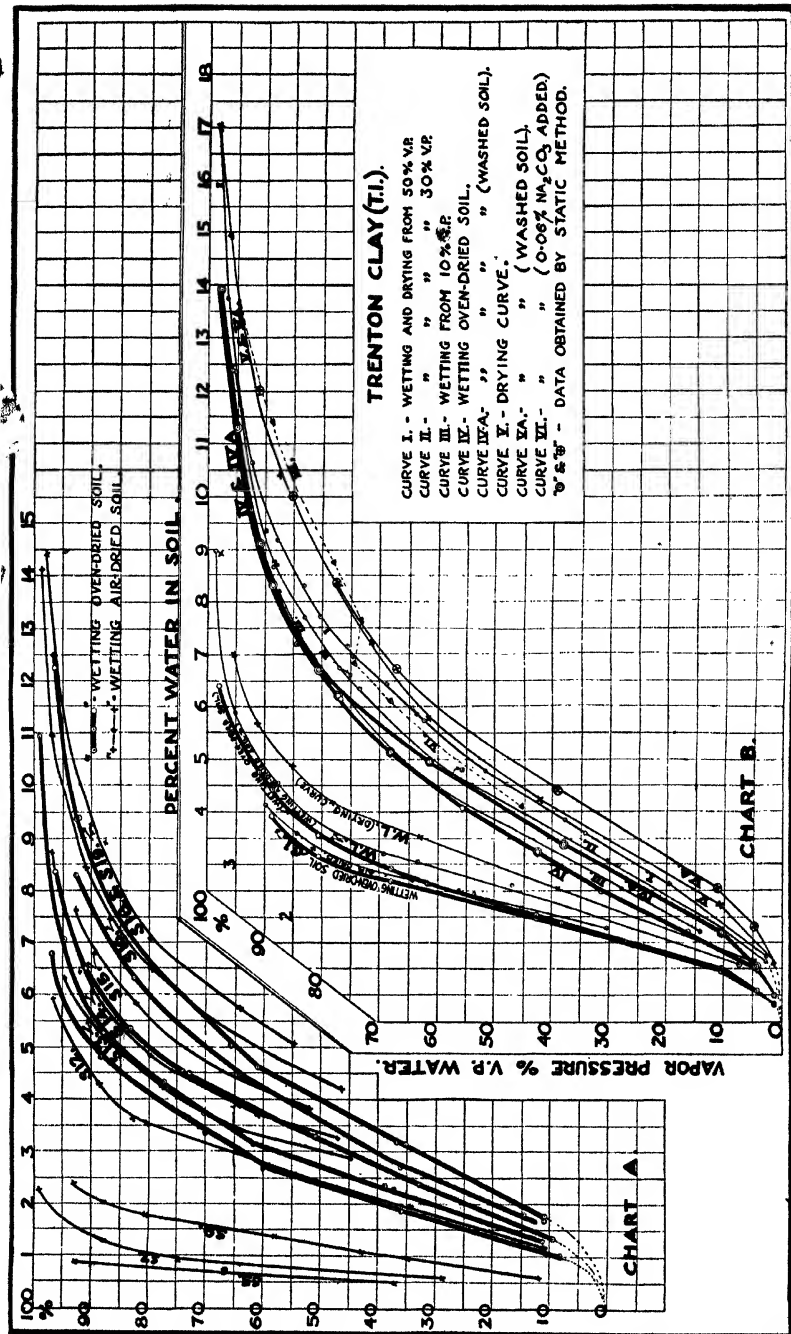
Fig. 2. Vapor Pressure Data: Chart A, Gardner's Separates; Chart B, Trenton Clay and Millville Soils

The curves illustrate the influence of the previous history of a soil on its vapor pressure and moisture relations

soils had been oven-dried before the vapor-pressure measurements were made, while the others had merely been air-dried. One vapor-pressure moisture diagram is therefore not sufficient to characterize a soil: the previous history must also be known. The work of Beaumont (3) indicates this fact also.

It will be seen that there is a tendency for the curves of soils S13 to S19 to change their direction rather suddenly at about 60 per cent vapor pressure, indicating an increased capacity for holding water. This tendency is not apparent after the curves have been shifted. Subsequent work on the Trenton clay, described below, shows that this condition is due to the fact that the soil had not always come to equilibrium with the added water when the vapor-pressure measurements were made, though duplicate determinations carried out on different days agreed closely. The drier the soil, the more slowly equilibrium is established, which accounts for the sharp angle at about 60 per cent vapor pressure. It is believed, however, that these curves are entirely comparable among themselves because they were worked out under comparable conditions.

Trenton clay

Since the vapor-pressure moisture function depends on the previous treatment, it seemed desirable to investigate it in greater detail. Since the available quantity of the heavier separates was limited, Trenton clay was selected as being likely to exhibit the characteristics of this function in considerable detail. Physical and chemical data on this soil have been given above.

A large, fresh, air-dried (about 50 per cent humidity) sample was put through a ½-mm. sieve and thoroughly mixed. Portions of this material were subjected to the following different treatments with the results shown in figure 2, chart B:

Curve 1. Wetting and drying by successive stages from 50 per cent vapor pressure.

Curve 2. Wetting and drying progressively from 30 per cent vapor pressure. Part of this material had previously been moistened to saturation by capillarity and part had been shaken with 2 per cent ammonia water, the two treatments giving identical results.

Curves 3 and 4. Wetting from 10 per cent vapor pressure and the oven-dried condition, respectively.

Curve 5. Drying by successive amounts from complete saturation with water.

Curve 6 Drying progressively after shaking with 0.025 per cent sodium carbonate (0.06 per cent on basis of dry soil).

Curves 4A and 5A. Subjecting washed soil to the wetting and drying processes, respectively, in the static process as described in the next section.

The dynamic method was used for all the determinations except curves 4A and 5A and a few measurements duplicating the conditions in curves 4 and 5. The latter data have been plotted on the graph as double-circled points and indicate satisfactory concordance between the two methods. Wetting the soil with liquid or gaseous water gives the same result, but the period of standing between the preparation of the sample and the measuring

of its vapor pressure seems to be important. In curve 1 this period was six months, but in the other work it was one to two months. For example, in curve 2 the period was six weeks. Two months later, three of the points on this curve were redetermined, as indicated by the small arrows. The driest soil (50 per cent vapor pressure) showed an appreciable shift, but equilibrium had apparently been reached with the others. This explains the shape of some of the curves obtained for the soil separates as noted above.

The data prove conclusively that the vapor-pressure moisture function depends on the previous history of the soil. Drying is particularly effective in raising the vapor pressure, that is, in making the texture appear coarser. The extent of this action depends on the extent of the drying. The mechanical analysis shows this action in a measure as well. It is thus possible for a sample of Trenton clay to stand in equilibrium with another sample of the same soil containing one-fourth to one-third more water.

Curves 1–4 are strikingly similar in shape, maintaining a constant distance between themselves and converging at high and very low vapor pressures. On the other hand, curves 5 and 6 seem to show that while the texture of the soil at high moisture contents may appear finer than that indicated by curve 1, below 70 per cent vapor pressure this curve represents the maximum dispersion for this soil in its natural state. The abnormal shape of curve 6 is probably to be explained by the flocculating action of the sodium carbonate when it became sufficiently concentrated by the evaporation of the water. This explanation will also apply to the difference between curves 4 and 4A and curves 5 and 5A. The method, therefore, gives promise of furnishing a quantitative means of studying the action of salts on the structure of soil and is being investigated further from this point of view.

The diverse group of soils

The other soils were all studied by the static method. Four series of observations were made. One set of samples was oven-dried and allowed to take up water in the desiccators (wetting curves). Another set was moistened by capillarity for two weeks and then allowed to dry out in the desiccators (drying curves). A larger sample of each soil was treated with water containing carbon dioxide and washed by decantation with distilled water until the colloid commenced to deflocculate. The material was then divided and both its wetting and drying curves determined. Except in the case of soils 993 and 994, which contained a large amount of soluble salt and soil T1, which has already been discussed, washing was without influence on the curves.

The results are given graphically in figure 3. The following anomalies are noticeable:

1. The drying curve of B5 is proportionately farther away from its wetting curve than is the case with the other soils.

2. The wetting curves of soils 170 and 172 converge at high vapor pressure and the drying curves actually cross.
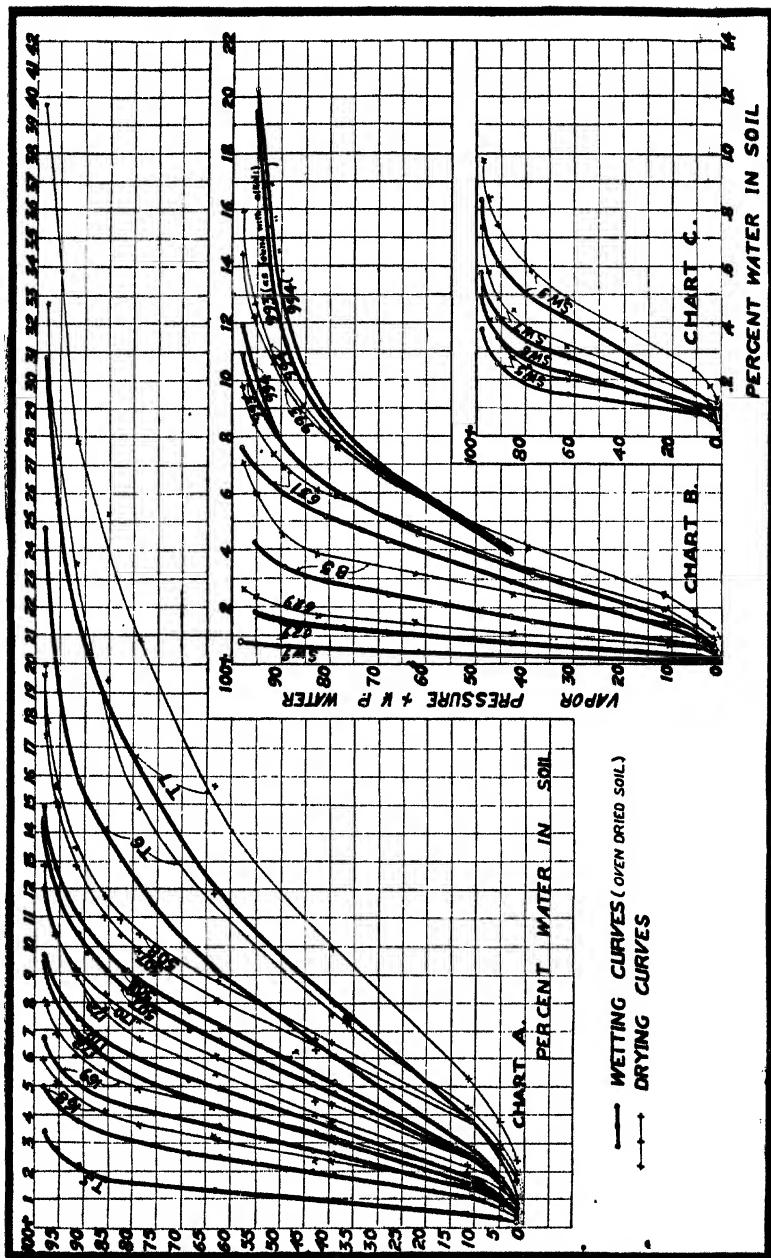
Fig. 3. Vapor Pressure Data for the Diverse Group of Soils

The effect of wetting from the oven-dry condition and drying from complete saturation with water is shown in each case

3. Soils 993 and 994 are almost coincident over most of their course, but they diverge appreciably on their upper portions. The wetting curves of these soils, as they were found impregnated with soluble salt (mainly sodium chloride) are also shown. The position of these curves indicates that all the salt is dissolved in the soil solution when more than 10 per cent moisture is present.

4. Even the coarse, well washed, separates show the inflection toward the origin at low vapor pressure (chart C, fig. 3).

<center>DISCUSSION</center>

Comparison of the vapor-pressure curves

It is evident from figure 3 that the drying curves are steeper than the wetting curves. Moreover, soils 508 and T7 belong to different families. In order to bring out the relationships existing between the curves, the moisture content of each soil has been divided by the corresponding value for either washed Trenton clay, or soil 508, on a number of different isobars. The results are given in tables 3 and 4. The ratios are approximately constant from 10 to 95 per cent vapor pressure for each soil treatment, and though different treatments change both the slope and position of the curves, the ratios are unaffected by these changes, that is, the curves are all shifted proportionately. Soil B5 is an exception, due perhaps to its higher organic matter content. The whole group of soils may therefore be divided into two families. A few individuals take a somewhat intermediate position, usually favoring one system more than the other.

It is difficult to assign a reason for the two families of curves. It may be noted, that the Trenton series is comprised for the most part of derivatives of Trenton clay together with the closely related Cache soils. On the other hand, the closely related Millville soils and the washed separates fall in the Abbott series. A chemical correlation seems hopeless. The carbonate content is apparently without significance because of its wide range in both families. A more probable explanation is to be found in the relative amounts of colloidal and silty material in the soils. In the last column of table 5, the surface of the particles larger than 0.1 micron has been divided by the total surface. In the Trenton series the quotient lies between 0.1 and 0.25, while in the Abbott it ranges from 0.25 to 1.0. The soils which give intermediate ratios, notably soils W. L. and S15, also occupy an intermediate position between the two families of curves. The only disturbing exception to this rule is soil T5 which is entirely very fine silt or coarse clay. It would seem therefore that when the colloidal surface is greatly in excess of the silty surface, the absorption at low pressures is repressed.

Vapor pressure and total surface

There is considerable evidence, as already pointed out, to indicate that the moisture contents of a series of soils on a given isobar are not necessarily proportional to their total surfaces. The present investigation offers a good opportunity for studying this question.

TABLE 3

Comparison of vapor-pressure curves—$\dfrac{H_2O \text{ in soil}}{H_2O \text{ in soil } T1}$ on isobars

WETTING CURVES, AIR-DRIED SOIL No. T1 = 1.00

VAPOR PRES-SURE	H2O IN T1	SOIL W.L.	SOIL G1	SOIL S5	SOIL S7	SOIL S9	SOIL S12	SOIL S13	SOIL s14	SOIL S15	SOIL S16	SOIL S18
per cent	per cent											
95	10.68	0.477	.....	.....	0.136	.....	0.440	0.515	0.608	.....	0.805	0.935
90	9.68	0.506	0.427	0.084	0.137	0.222	0.457	0.562	0.630	0.712	0.836	0.955
85	8.50	0.491	0.426	0.091	0.136	0.223	0.443	0.571	0.625	0.718	0.833	0.937
80	7.60	0.487	0.429	0.097	0.132	0.228	0.456	0.575	0.633	0.724	0.850	0.924
70	6.46	0.496	0.437	0.103	0.132	0.236	0.480	0.570	0.648	0.721	0.859	0.950
60	5.50	0.534	0.468	0.109	0.140	0.247	0.498	0.594	0.665	0.751	0.885	0.975
55	5.10	0.540	0.472	0.112	0.143	0.251	0.503	0.600	0.674	0.760	0.892	0.985
Mean 55–95		0.504	0.443	0.099	0.137	0.235	0.468	0.570	0.640	0.731	0.851	0.951

WETTING CURVES, OVEN-DRIED SOIL No. T1 = 1.00

VAPOR PRES-SURE	H2O in T1	SOIL W.L.	SOIL G1	SOIL 508	SOIL 993	SOIL 994	SOIL T5	SOIL T6	SOIL T7	SOIL S13	SOIL S14	SOIL S15	SOIL S16	SOIL S18
per cent	per cent													
95	11.05	0.500	.....	1.14	0.852	0.905	0.256	1.71	2.24	0.540	0.644	0.683	0.842	0.952
90	8.70	0.517	0.460	1.24	0.909	0.920	0.253	1.78	2.38	0.571	0.642	0.723	0.864	0.978
85	7.50	0.525	0.460	1.30	0.940	0.940	0.260	1.85	2.46	0.602	0.654	0.741	0.885	0.980
80	6.80	0.513	0.452	1.33	0.941	0.941	0.258	1.83	2.47	0.607	0.670	0.738	0.874	0.960
70	5.68	0.532	0.475	1.39	0.931	0.931	0.256	1.82	2.43	0.594	0.651	0.756	0.870	0.950
60	4.80	0.532	0.508	1.45	0.935	0.935	0.265	1.81	2.42	0.587	0.643	0.783	0.878	0.980
50	4.15	0.541	0.517	1.45	0.937	0.937	0.268	1.77	2.35	0.582	0.663	0.782	0.865	0.956
35	3.16	0.563	0.550	1.52	0.965	0.965	0.272	1.80	2.34	0.580	0.686	0.781	0.870	0.975
20	2.28	0.567	0.547	1.53	0.962	0.962	0.272	1.78	2.33	0.601	0.704	0.780	0.885	0.977
10	1.68	0.578	0.547	1.49	0.950	0.950	0.268	1.64	2.18	0.630	0.732	0.802	0.893	1.000
Mean 10–95		0.537	0.502	1.38	0.933	0.938	0.264	1.78	2.36	0.589	0.667	0.757	0.873	0.970

DRYING CURVES No. T1 = 1.00

VAPOR PRESSURE	H2O IN T1	SOIL W.L.	SOIL G1	SOIL 508	SOIL 993	SOIL 994	SOIL T5	SOIL T6	SOIL T7
per cent	per cent								
98	19.4	0.470	....	1.05	0.747	0.825	....	1.69	2.05
95	14.5	0.461	....	1.07	0.835	0.856	....	1.85	2.28
90	11.25	0.471	....	1.15	0.897	0.920	....	1.93	2.36
85	9.87	0.481	....	1.18	0.901	0.922	....	1.82	2.38
80	8.80	0.490	....	1.21	0.892	0.915	....	1.76	2.44
70	6.97	0.537	....	1.36	0.947	0.969	....	1.83	2.50
60	5.95	0.565	....	1.43	0.958	0.975	....	1.83	2.40
50	5.13	0.577	....	1.48	0.955	0.975	....	1.79	2.34
35	4.14	0.572	....	1.49	0.960	0.975	....	1.70	2.22
20	3.15	0.570	....	1.52	0.960	0.980	....	1.68	2.17
10	2.43	0.571	....	1.54	0.965	0.985	....	1.65	2.06
5	1.85	0.615	....	1.54	·0.965	1.000	....	1.62	2.02
Mean 10–95		0.530	....	1.34	0.920	0.947	....	1.78	2.32

TABLE 2

Comparison of vapor-pressure curves $\dfrac{H_2O \text{ in soil}}{H_2O \text{ in soil } 508}$ on isobars

WETTING CURVES—OVEN-DRIED SOIL (508 = 1.00)

VAPOR PRESSURE	H₂O in 508	SOIL SW5	SOIL SW6	SOIL SW7	SOIL SW9	SOIL G1	SOIL W.L.	SOIL B5	SOIL 165	SOIL 169	SOIL 170	SOIL 172	SOIL 629	SOIL 631	SOIL 507
per cent	per cent														
98	14.95	0.0255	0.0335	0.0390	0.0560	....	0.426	....	0.340	0.452	0.650	0.630	....	0.522	0.970
95	12.55	0.0255	0.0335	0.0390	0.0550	....	0.430	0.332	0.350	0.464	0.680	0.630	0.141	0.550	0.950
90	10.82	0.0227	0.0315	0.0384	0.0545	0.369	0.417	0.321	0.340	0.470	0.670	0.615	0.140	0.558	0.932
85	9.78	0.0213	0.0316	0.0378	0.0550	0.354	0.402	0.320	0.343	0.474	0.666	0.604	0.143	0.562	0.928
80	9.02	0.0205	0.0305	0.0388	0.0560	0.342	0.382	0.320	0.344	0.480	0.677	0.597	0.142	0.567	0.920
70	7.90	0.0203	0.0306	0.0397	0.0575	0.342	0.376	0.317	0.343	0.500	0.690	0.597	0.142	0.560	0.930
60	6.95	0.0207	0.0312	0.0403	0.0580	0.350	0.369	0.317	0.352	0.503	0.690	0.603	0.138	0.552	0.932
50	6.02	0.0219	0.0320	0.0412	0.0588	0.358	0.374	0.316	0.360	0.506	0.697	0.602	0.135	0.540	0.945
35	4.80	0.0239	0.0323	0.0417	0.0582	0.362	0.371	0.292	0.374	0.502	0.682	0.594	0.131	0.525	0.940
20	3.48	0.0278	0.0345	0.0430	0.0582	0.370	0.384	0.302	0.379	0.505	0.680	0.588	0.131	0.518	0.940
10	2.51	0.0334	0.0386	0.0470	0.0595	0.340	0.356	0.299	0.397	0.516	0.685	0.595	0.132	0.518	0.947
5	1.64					0.384	0.384	0.366	0.408	0.542	0.670	0.598	0.152	0.550	0.945
Mean	10–95	0.0238	0.0326	0.0407	0.0570	0.354	0.396	0.314	0.358	0.492	0.682	0.602	0.138	0.545	0.936

DRYING CURVES (508 = 1.00)

VAPOR PRESSURE	H₂O in 508	SOIL SW5	SOIL SW6	SOIL SW7	SOIL SW9	SOIL G1	SOIL W.L.	SOIL B5	SOIL 165	SOIL 169	SOIL 170	SOIL 172	SOIL 629	SOIL 631	SOIL 507
98	20.0	0.0265	0.0310	0.0370	0.049	....	0.445	0.360	0.297	0.403	0.602	0.641	0.135	0.493	0.950
95	15.5	0.0258	0.0326	0.0370	0.0535	....	0.431	0.387	0.330	0.440	0.658	0.658	0.149	0.545	0.955
90	12.95	0.0251	0.0324	0.0363	0.0548	....	0.410	0.356	0.343	0.460	0.687	0.665	0.148	0.545	0.950
85	11.67	0.0238	0.0326	0.0364	0.0557	....	0.407	0.348	0.343	0.461	0.694	0.646	0.148	0.548	0.945
80	10.65	0.0240	0.0320	0.0366	0.0565	....	0.405	0.356	0.350	0.470	0.705	0.640	0.150	0.562	0.945
70	9.50	0.0234	0.0306	0.0366	0.0558	....	0.394	0.361	0.354	0.477	0.702	0.635	0.153	0.557	0.943
60	8.54	0.0236	0.0310	0.0369	0.0554	....	0.394	0.360	0.355	0.480	0.691	0.620	0.153	0.548	0.937
50	7.58	0.0238	0.0317	0.0369	0.0565	....	0.391	0.360	0.356	0.484	0.675	0.600	0.154	0.533	0.937
35	6.17	0.0244	0.0317	0.0377	0.0577	....	0.384	0.362	0.357	0.481	0.655	0.574	0.157	0.526	0.937
20	4.77	0.0266	0.0325	0.0388	0.0597	....	0.376	0.360	0.369	0.475	0.655	0.566	0.161	0.523	0.947
10	3.74	0.0294	0.0337	0.0404	0.0613	....	0.372	0.371	0.390	0.480	0.655	0.567	0.168	0.502	0.962
5	2.83	0.0328	0.0417	0.0465	0.0635	....	0.409	0.399	0.399	0.480	0.643	0.594	0.176	0.498	0.955
Mean	10–95	0.0250	0.0321	0.0374	0.0567	....	0.396	0.362	0.355	0.471	0.678	0.617	0.154	0.539	0.945

The soil surfaces have been calculated from the data in figure 1, assuming the particles to be spherical in shape. The assumptions which were made in

TABLE 5

Comparison of soil surfaces found by mechanical analysis and calculated from vapor-pressure data

SOIL NUMBER	TOTAL SURFACE PER GM.		SURFACE OF PARTICLES LARGER THAN						SURFACE OF PARTICLES >0.1 μ + TOTAL SURFACE
			0.1 micron radius			0.25 micron radius			
	Found	Calculated	Part disregarded	Found	Calculated	Part disregarded	Found	Calculated	
	sq. meters	sq. meters	per cent	sq. meters	sq. meters	per cent	sq. meters	sq. meters	
Trenton series									
S5	0.69	1.10	1.1	0.117	0.163	2.1	0.064	0.086	0.170
S7	0.77	1.52	1.5	0.141	0.226	2.2	0.107	0.129	0.183
S9	1.20	2.59	2.0	0.300	0.384	3.6	0.184	0.203	0.250
S12	3.14	5.20	6.6	0.578	0.606	9.9	0.340	0.408	0.184
S13	4.30	6.33	8.3	0.826	0.955	13.8	0.449	0.505	0.192
S14	4.36	7.10	8.6	0.930	1.075	14.2	0.526	0.570	0.212
S15	4.61	8.12	9.5	1.17	1.23	19.2	0.638	0.649	0.254
S16	8.34	9.45	17.6	1.45	1.42	27.5	0.720	0.750	0.174
S18	10.4	10.6	23.0	1.57	1.58	33.5	0.810	0.835	0.151
T5	1.36	2.93	0	1.36	0.435	0	1.36	0.230	1.00
T6	15.8	19.8	32.0	3.30	2.94	61.2	1.23	1.56	0.209
T7	24.8	26.0	56.0	3.02	3.86	92.0	0.251	2.04	0.122
993	6.82	8.77*	13.0	0.881	1.30*	17.2	0.579	0.69*	0.129
994	9.43	9.45*	19.2	1.117	1.40*	26.8	0.675	0.74*	0.120
T1	11.1	(11.1)	22.1	1.65	(1.65)	33.1	0.872	(0.872)	0.149
Abbott series									
SW5	0.0380	0.16	0	0.0380	0.046	0	0.0380	0.026	1.00
SW6	0.0458	0.21	0	0.0458	0.061	0	0.0458	0.035	1.00
SW7	0.0569	0.25	0	0.0569	0.075	0	0.0569	0.041	1.00
SW9	0.0884	0.37	0	0.0884	0.112	0	0.0884	0.063	1.00
G1	1.94	2.31	3.0	0.620	0.685	6.4	0.384	0.389	0.320
W.L.	3.59	2.59	7.3	0.628	0.77	10.7	0.375	0.435	0.175
B5	1.26	2.21	2.3	0.420	0.655	4.6	0.266	0.370	0.333
168	0.976	2.32	1.2	0.442	0.69	2.0	0.395	0.403	0.453
169	1.36	3.15	2.0	0.644	0.93	4.3	0.481	0.530	0.473
170	2.78	4.45	4.0	1.12	1.32	10.3	0.709	0.748	0.403
172	4.11	3.98	6.8	1.26	1.18	16.0	0.647	0.670	0.307
629	0.886	0.95	1.4	0.218	0.283	2.3	0.157	0.160	0.408
631	4.16	3.54	9.1	1.005	1.05	18.5	0.337	0.579	0.250
507	4.28	6.15	5.6	1.78	1.82	15.5	1.17	0.103	0.415
508	6.54	(6.54)	10.7	1.94	(1.94)	23.5	1.10	(1.10)	0.297

* Calculated by using ratios of vapor-pressure curves on isobars above 95 per cent.

estimating the size of the particles in the mechanical analysis have been discussed elsewhere (11). The principal uncertainty in the evaluation of the total surface is probably involved in the extrapolation of the distribution

curves. The results are given in table 5. The total surfaces have also been calculated by multiplying the values found for Trenton clay and 508, by the ratios of the vapor-pressure curves given in tables 3 and 4. The theoretical quantities are generally considerably larger than those determined experimentally.

Similar calculations have been made of the surface of the particles larger than 0.1 micron and also 0.25 micron radius, disregarding completely the smaller material in each case. As the amount of soil surface considered increases, the ratio of the theoretical to the actual surface increases. Except in unusual soils, this ratio becomes unity when the comparison is made on the basis of the particles larger than a dimension between these limits. This applies even to soils 170 and 172, in which case the heavier soil exhibits the lower hygroscopicity except at high vapor pressure. With the Trenton separates, more surface must be compared: the experimental values for the surface larger than 0.05 micron, in T6 and T7, are 5.27 and 6.48 square meters per gram, while the calculated values are 5.10 and 6.70, respectively. T5 requires the consideration of the surface of Trenton clay down to 0.02 micron.

Since it is really the smaller material which is responsible for most of the absorption, the relationships in table 5 must mean that the absorptive surface is usually more efficient in the lighter soils. The fact that these conditions obtain with substances of different chemical composition as well as with chemically related soils may be interpreted to indicate that the absorption is influenced mainly by the size and arrangement of the particles.

THICKNESS OF THE WATER FILM

The thickness of the water film deduced from the data in this paper ranges from molecular dimensions (about 5×10^{-7} mm.) at 1 per cent vapor pressure to about 2×10^{-5} at 98 per cent. These values are of the same order of magnitude as those found by Odén (14). Unless the estimated surface of the soil is too small it may be stated, contradicting the theory of Rodewald and Mitscherlich, that the water film is at least one molecule thick in an atmosphere of 1 per cent humidity instead of 96 per cent, as the "hygroscopicity" theory demands.

The following is suggested as the mechanism of adding water to an ovendried soil. The first layer of water molecules is held so tenaciously that its vapor pressure is very low. A few succeeding layers cause greater increments of the vapor pressure and produce the part of the curve which is concave upward. Then the addition of more water results in a large increase in vapor pressure and the straight portions of the curves are obtained. The capillary spaces are probably commencing to fill at this stage. Finally, as the water wedges grow in size, it requires larger amounts of moisture to produce a given increment of the vapor pressure, and the curves are concave downward.

Table 5 seems to show that the relative power for absorbing water in a comprehensive series of soils is measured by the relative surfaces of the particles larger than 0.1 to 0.25 micron radius, independently of the smaller colloidal material, whereas it is really the latter which is responsible for most of the absorption.

This condition can probably be explained by the concept of the colloid-coated particle, such as has been postulated by Keen (12) to explain evaporation phenomena and by Comber (5, 6) to explain flocculation phenomena. On this view, the soil grains are enlarged by being coated with a jelly-like covering of colloidal material which collapses on drying to form a layer difficultly permeable to water, with a moisture gradient from the core to the outside. The total amount of water associated with this aggregate is therefore less than if its component particles were completely dispersed. Thick coatings would show these effects more noticeably than thin coverings, as is indicated by the two families of curves. The colloidal structure is partially destroyed by dehydration, and the coating becomes to some extent in effect a part of the core. This condition is slowly reversed by the addition of water, the speed and extent of the reversal depending upon the amount of water added. It may be remarked in this connection that in carrying out the mechanical analysis, when suspensions are evaporated which contain particles of low colloidal dimensions only, this material adheres to the weighing bottles as a vitreous mass which can not be removed without the greatest difficulty, whereas if coarser grains are also present in the suspension the weighing bottles can be easily cleaned.

This theory also explains the behavior of the soil in the mechanical analysis. In our method (11) and also in that of Odén (15) only one sedimentation is made. Accordingly, if the dispersion in the suspension is not complete at the start the results will indicate a coarser texture in the soil than really exists. The data given in the insert of chart C, figure 1 show that the soil samples did not always remain in contact with the deflocculating solution long enough (one or two days) to effect complete dispersion before the sedimentation commenced. This was invariably the case if the soil samples had been thoroughly air-dried or oven-dried. This error would not affect those methods which employ repeated gravity sedimentations because the colloids would be eventually peptized, but it might influence the more rapid centrifugal methods.

SUMMARY

The vapor-pressure-moisture curves of a comprehensive series of soils ranging from fine sands to tight clays and from highly calcareous to highly silicious materials have been investigated at comparatively low moisture contents, with special reference to the influence on the curves of wetting and drying the soils. Complete chemical and mechanical analyses have been made on these materials. It has been shown that:

1. The dynamic and static methods of measuring vapor pressure give identical results.

2. The chemical composition of these soils, which are generally deficient in organic matter, is a minor factor in its influence on the absorption of water.

3. The vapor-pressure-moisture function depends on the previous history of the soil. Drying is particularly effective in raising the vapor pressure at a given moisture content, the extent of this action depending on the completeness of the drying. This effect is reversed by protracted contact with moderate amounts of water or shorter contact with excess of water. The mechanical analysis also indicates that drying the soil makes the texture appear coarser.

4. If comparable vapor-pressure-moisture curves are considered all the soils may be divided into two groups, in each of which the relative amounts of hygroscopic water remain nearly constant over the range from 10 to 95 per cent of the vapor pressure of water. Changes in the slope and position of the curves due to wetting and drying treatments do not change the relative hygroscopicities. The existence of the two families of curves is probably accounted for by the relative amounts of colloidal and silty material.

5. These ratios of the hygroscopic water agree closely with the ratios of the surfaces, as determined by mechanical analysis, of the particles larger than about 0.1 to 0.25 micron radius, disregarding the smaller material.

6. The thickness of the moisture film agrees well with the corresponding value calculated from Odén's data (14) but is much smaller than the value found by Patten and Gallagher (16). The theory underlying the method of Rodewald and Mitscherlich (17) for estimating the total surface of a soil from the "hygroscopicity" is not confirmed.

7. The vapor-pressure-moisture function will probably furnish a means of studying the influence of soluble salts on the structure of soils.

8. The experimental data in this paper seem to confirm the theory of the colloid-coated particle developed by Keen (12) and Comber (5, 6).

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EXPERIMENTS WITH BACTERIAL SOIL FERTILIZING PREPARATIONS

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Soil inoculation came as a result of purely empirical observations, long before the discovery of the nodule microbe (*Bacillus radicicola*), and furnished a foundation for bacterial soil fertilizing preparations.

A German farmer *August Salfeld* (16), who was forced to cultivate an infertile soil, for the growth of legumes, conceived the thought of "manuring" with soil from fields which had produced good harvests of the same plants. The results were satisfactory and this original way of fertilizing became rather widespread in Germany, Holland, Denmark and other countries; at times this method gave even better results than saltpeter applications. At first the beneficial effects were attributed to the organic material of the added soil, but after the discovery of the nodule microbe by Hellrigel and Wilfarth (6), it was clear that they were due to an infection of *Bacillus radicicola*. Later Nobbe and Hiltner (15) suggested soil inoculation with pure cultures of the nodule microbes. Thus the first bacterial soil fertilizer, Nitragin, was introduced. It was cultures of *Bacillus radicicola* grown on gelatin. Cultures were prepared at the chemical plant in Höchst for clover, alfalfa, lupine, vetch and other legumes.

The first experiments with this fertilizer gave variable results. Nevertheless the inventors of Nitragin persevered and the study of its merits was transferred to the laboratory. The failures were at first attributed to the artificial environment of the microbes and to the excretions of the germinating seeds.

In view of this, Hiltner and Störmer (8) prepared "Nitragin" in the form of pure cultures of *Bacillus radicicola* in a liquid medium. The medium consisted of a 2 per cent peptone solution or skimmed milk.

Extensive experiments with this preparation in Bavaria gave very good results, only 17 per cent of the experiments having been negative. These experiments attracted the attention of investigators throughout the world. In England Bottomley (1) devised a preparation known as "Nitrobacterin." In America Moore (14) prepared "Nitroculture."

Bottomley conducted field experiments in England; the results were fairly good; he obtained increases of 25–50 per cent; only 20 per cent of the experi-

ments were a failure. Moore's "Nitroculture" was tested out in the United States on a much larger scale; about 2500 experiments were conducted in the different states. The experiments gave quite favorable results. Crop increases were obtained of 20-80 per cent. About 24 per cent of all the experiments were unsuccessful. Simultaneously experiments were set up by Vogel (20) in Europe and in Africa; about 5220 preparations were tried; all the experiments gave good results. Hiltner (7) organized in Germany about 300 experiments, 70 per cent of which were successful. Stutzer (19) obtained good results in 75 experiments out of 100. The underlying principles were not understood and the results obtained were purely empirical. The point of view of the investigators was that soil inoculation depends chiefly upon the quality of the preparation and preserving the vitality and activity of the bacteria. The sponsor of this view was Simon (18) who originated "Azotogen," a culture of *Bacillus radicicola* in a sterile soil, manured with lime. All the efforts of the investigators at that time were directed toward technical perfection of the preparations and the methods of application.

Kühn (13) prepared "solid Nitragin" consisting of cultures of *Bacillus radicicola* in sterile soil. Experiments with these fertilizers conducted by Feilitzen (4) on peat soil gave favorable results.

Experiments conducted by the author with the same preparations in vessels with peat soils, manured with lime, Thomas slag and potassium salts gave equally good results. Nevertheless, "Azotogen" and "solid Nitragin Kühn," even when of good quality and freshly prepared, had some defects; they did not represent pure cultures of *Bacillus radicicola* and dried out very quickly.

The next, most interesting point in the history of the application of bacterial soil fertilizers, pertained to the question of the need for bacterial inoculation of soils, that normally contain nodule microbes. The investigations of Duggar and Proucha (2) in a way answer this question. They have shown that *Bacillus radicicola* inoculated in sterile soil multiplies intensively; on the other hand, when this same sterile soil is mixed with non sterile soil, the propagation of the microbe slackens in proportion to the quantity of the added non-sterile soil. These experiments thus indicate that the nodule microbes under natural conditions cannot compete with other soil bacteria, progressively dying out and decreasing in numbers. This has been confirmed by Kalantarov (9). The author has also noted the rapid disappearance of the nodule microbes in the soil after harvesting legumes. It is easy to isolate nodule microbes from such a soil by using a medium specific for *Bacillus radicicola*, namely dextrose agar. The organism develops in characteristic ductile colonies similar to drops of wax, entirely different from the colonies of other microbes, which grow but in a very limited way in this specific medium.

The failure of the nodule microbes to compete with the typical soil bacteria depends, so to say, upon their parasitic existence on the plants, and therefore the soil is not a normal medium for them.

Direct observations on the growth of legumes show that under ordinary

conditions there may be the complete disappearance of the nodule microbes from the soil and consequently the growth of legumes without nodules. An acid reaction of the soils in the northern, north western and north eastern districts of Russia inhibits nodulation of legumes there. Investigations made on the root system of legumes in some parts of the Porchovsky district, government of Pskov, showed at times that even in the case of good harvests,

TABLE 1

Effect of various forms of inoculants on growth of legumes in sand cultures

	WEIGHT OF AIR-DRIED PLANTS			
	Clover		Vetch	
TREATMENT	Duplicate determinations	Average	Duplicate determinations	Average
	gm.	*gm.*	*gm.*	*gm.*
Control nitrates...................	23.3 21.6	22.45	25.22 20.91	23.05
Control without nitrate.............	2.7 1.8	2.25	2.9 2.1	2.5
Pure cultures of *B. radicicola*........	17.00 14.30	16.05	18.9 13.87	16.38
Azotogen.	13.8 11.2	12.5	15.6 12.4	14.0
Nitragin........................	12.1 8.9	10.5	13.2 8.87	11.0
Nodules........................	10.2 6.7	8.45	11.5 0.0	11.5

the nodules were absent, or present in such small numbers that they could not be of any significance to the plants. The roots have a weak development and one must conclude that in such cases the legumes draw their nitrogen not from the atmosphere, but from the soil; that is, instead of enriching, they exhaust the soil of its nitrogen. If we consider the enormous extent of such acid soils in Russia, it is easy to imagine the yield losses.

The experiments of Gerlach and, Vogel (5), Alfred Koch (11, 12), West (21) and others give but indirect information as to the conditions favoring the nitrogen-fixing bacteria: sufficient mellowing of the soil, fertilization with organic substances, which serve as a source of energy for the nitrogen fixing organisms, liming, etc.

TABLE 2

Comparison of crop yields on inoculated and uninoculated plots

EXPERIMENT NUMBER	NAME OF EXPERIMENTER AND PLANTS USED	SOIL	FERTILIZERS* PER DESIATINA†				Size of plot	CROP PER PLOT		INCREASE OF CROP
			Super-phosphate	Thomas slag	K₂SO₄	CaO		Control	Inoculated	
			poods†	poods	poods	poods	acres	poods	poods	per cent
	Zhicharewa:									
1	Vetch	Tzernozeme mixed with clay	....	...	....	....	0.8	72	95	31.9
2	Vetch		....	...	....	50	0.8	72	87.5	21.5
3	Vetch	Podzol sandy loam, swampy	....	24	12	....	0.8	138	288	108.7
	Lashkewitch:									
4	Vetch	Podzol sandy loam, swampy	....	34	24	....	0.8	104	186	78.8
5	Vetch		....	34	24	....	0.8	141	193	37
	Shkokman:									
6	Vetch	Sandy loam and loamy sand	....	24	....	....	0.8	75	90	20
	Petrovsky:									
7	Clover		....	24	12	150	2.7	196	256	30.6
8	Clover		....	24	12	....	2.7	208	204	....
9	Clover	Sandy loam with loamy subsoil	....	:	....	....	2.7	144	184	27.8
10	Vetch		....	:.	12	....	2.7	71	127	78.6
11	Vetch		....	24	12	....	2.7	108	131	21.3
12	Vetch		....	24	12	150	2.7	172	191	11
	Gloushkoff:						sq. meters	pounds	pounds	
13	Clover		....	:.	....	....	38.3	30	40	33.3
14	Clover		....	24	....	....	38.3	31	43	38.3
15	Clover	Podzol sandy loam with red clay subsoil	....	:.	....	100	38.3	32	41	28.0
16	Vetch		.:.	:.	....	....	38.3	35	43	23.0
17	Vetch		24	:.	....	....	38.3	37	48	29.7
18	Vetch		....	:.	....	100	38.3	35	48	37.0

No.	Crop	Soil									
Pissareff:											
19	Vetch	Sandy loam poor in				180	4.8	11.22	14.0	24.0
20	Vetch	humus				180	4.8	13.0	14.15	9.4
							acres	*poods*	*poods*	*poods*
Stahl:											
21	Vetch	Loamy sand	22.5		13.5		2.7	640	682	6.5
22	Vetch		22.5		13.5		2.7	630	718	14
23	Clover		22.5		13.5		2.7	536	546	....
24	Clover	Sandy loam	22.5		13.5		2.7	570	514	....
25	Vetch			24			2.7	424	518	22.1
26	Vetch			24			2.7	376	484	28.7
Engelgard Exp. St.							*sq. meters*	*pounds*	*pounds*	
27	Vetch						24.6	16.4	25.6	56.1
28	Vetch						24.6	21.7	27.0	30.4
29	Vetch						24.6	18.2	24.4	34.0
30	Vetch						24.6	18.7	19.0	....
31	Vetch		3				24.6	29.8	29.9	....
32	Vetch	Sandy loam with forest	3				24.6	19.7	26.7	35.5
33	Vetch	litter	4		4		24.6	26.5	31.0	17.0
34	Vetch		4		4		24.6	25.8	29.5	14.3
35	Vetch						24.6	29.7	38.4	29.3
								gm.	*gm.*	
36‡	Vetch		{1.8 gm. NaPO₄}				....	40.05	51.3	28.2
37‡	Vetch				0.48 gm.K		....	40.15	44.8	11.6
Allen:							*acres*	*poods*	*poods*	
38	Vetch	Sandy loam					0.5	41	50.7	23.7

* Nitrogenous fertilizers were used in experiment 3 in the form of (NH₄)²SO₄ (32 kgm. per acre) and in experiments 7, 12, 51 and 53 in the form of NaNO₃ (32 kgm. per acre).

† Pood = 16.38 kgm.; one Russian pound = 0.41 kgm.; desiatina = 2.7 acres.

‡ Experiments conducted in pots.

TABLE 2—Continued

| EXPERIMENT NUMBER | NAME OF EXPERIMENTOR AND PLANTS USED | SOIL | FERTILIZERS PER DESIATINA† | | | | Size of plot | CROP PER PLOT | | INCREASE OF CROP |
| | | | Super-phosphate | Thomas slag | K_2SO_4 | CaO | | Control | Inoculated | |
			poods†	poods	poods	poods	acres	poods	poods	per cent
	Benevolensky:									
39	Vetch, Oats	Slightly decomposed peat soil with a high ash content	……	24	15	……	1.0	390	438	12.3
40	Vetch, Oats		……	24	15	……	0.4	270	348	25.2
	Reineck:						sq. meters	pounds	pounds	
41	Clover	Virgin clay	……	……	……	……	28.7	187	205.5	10.0
42	Clover		24	……	12	……	28.7	……	216.3	29.3
43	Clover	Old neglected hot beds, not used	……	……	……	……	4.8			
44	Vetch		……	……	……	……	4.8		No account of the crop was made. The plant on the inoculated plots seemed denser	
45	Lupine		……	……	……	……	4.8			
	Bachteeva:							sheaves§	sheaves	
46	Vetch	Drained peat bog	……	24	12	150	9.6	11.5	16.5	43.5
47	Clover		……	24	12	150	9.6	6.6	10.3	56.0
	Sawinoff:							poods	poods	
48	Clover	Drained peat bog	……	24	24‖	200	9.6	248	395	59.2
49	Vetch		……	24	24‖	200	9.6	480	500	……
	Makrinoff:									
50	Clover	Virgin sand	……	24	12	150	0.5	3/8	4/8	33.3
51	Clover		……	24	12	150	0.5	6/8	7/8	17
52	Vetch		……	24	12	150	0.5	1/2	3/4	50
53	Vetch		……	24	12	150	0.5	5/8	7/8	40

§ The crop was estimated by standard sheaves from 5 square meters.
‖ Wood ashes.

Thus, it may readily be seen that with out present knowledge the cardinal questions are:

1. What are the causes of failure of the bacterial soil fertilizers?

2. Can soil inoculation be used widely in our common farm practices?

These two questions led to the investigations reported here. Vessels of 5-kgm. capacity were filled with sand which had been previously ignited and washed with HCl. Knop's culture solution without saltpeter was used for all cultures except the controls which received also the saltpeter. The vessels after planting were kept in the greenhouse for 2.5 months. "Azotogen," "Nitragin Kuhn," nodules and pure cultures of *B. radicicola* prepared by the author were used in this experiment. Table 1 gives the plan and the results of the experiment.

TABLE 3

Effect of various treatments on number of nodules

EXPERIMENT NUMBER	PLANTS	TREATMENT	AVERAGE NUMBER OF NODULES ON FIVE ROOTS	
			Non-inoculated	Inoculated
16	Vetch	Without manure	27	47
13	Clover	Without manure	41	100
1	Vetch	Without manure	32.6	36.8
2	Clover	Without manure	45.4	81.8
2	Clover	Without manure	46.0	....
18	Vetch	Lime	36.0	52
15	Clover	Lime	58.0	108
3	Vetch	Lime	53.0	89
17	Vetch	Superphosphate	21.0	49
14	Clover	Thomas slag	58.0	98
3	Clover	Lime with liquid dung	50.4	112.2
3	Vetch	Lime with liquid dung	67.6	127.8

The preparations used in the sand cultures were then tried out in field experiments. The results were rather obscure. Many of the experiments proved the value of inoculation, while others did not.

The experiments were conducted in various parts of the country but unfortunately some of them, especially those in the war zone, were lost. In all the experiments an effort was made to supply calcium, phosphorus and potassium to the soil for the benefit of the nodule forming bacteria, avoiding acid phosphate, since it imparts temporarily an acid reaction to the soil. It is known that an acid reaction inhibits the development of nodule bacteria; even root excretions, usually of an acid nature, retard the growth of the nodule bacteria.

The results obtained may be summed up as follows:

1. Increase in crop yields, due to inoculation as presented in table 2.

2. Increase of the number of nodules on the inoculated plots as shown in table 3. •

3. Increase in weight of roots of the infected plants.

Table 2 shows that generally the greatest success with inoculation was obtained with those experiments in which the alkaline manures were applied: Thomas slag, or lime, or both, as in experiments 3–8. Very instructive are experiments 21–26 made by Stahl. Here the application of acid manures on loamy soil (superphosphate, potassium salt in the experiments 21–24) gave no result whatever, on the contrary the application of Thomas slag on the same soil (experiments 25–26) showed at once a definite beneficial effect. The unfavorable results may be ascribed to the acid reaction of the northwestern and eastern soils of Russia on one hand and on the needs of calcium by the legume bacteria on the other hand. It may be inferred therefore, that experiments with soil inoculants without supplying calcium, phosphorus and potassium fertilizers of a neutral or alkaline reaction are bound to fail. For this reason probably the experiments of Severin (17) failed.

Table 2 also shows that in some cases (13–16, 27–30–32) favorable results were obtained even on those plots where no manures were added. Upon examination it was found that these plots were supplied with fertilizers in previous years.

The success of the soil inoculation without preliminary manuring with lime, phosphorus and potassium salts in western Europe may be explained by the superior cultivation of the soil.

Saltpeter manuring gave interesting effects. It is known that additions of saltpeter in artificial cultures has an unfavorable effect on the nitrogen fixing capacity of the microbes, reducing or completely suppressing it; the results in the field corroborated these observations. When the soil was treated with 6 poods of saltpeter per desiatina inoculation had no effect. The crop did not increase and the nodules did not appear on the roots. Figs. 3 and 4 represent roots from plots which did not receive saltpeter (exp. 50–52). Plate 1 represents roots from plots manured with saltpeter (exp. 51–53). The roots are bare, almost devoid of nodules and with thin ramifications.

These results corroborate in a way the work of Düggeli (3), who found that saltpeter inhibited the growth of azotobacter and decreased the numbers of them as compared with those plots which received no saltpeter. Table 3 shows the increase of nodules on the roots of infected plants in comparison with noninfected ones. It is well to record the fact that the increase in number of the nodules is even more constant than the increase in the crop.

This table also shows that the manuring with lime and Thomas slag had a beneficial action on nodulation. Manuring with superphosphate in certain experiments (exp. 17) the number of nodules was lowered even in comparison to the plots which had not received mineral manuring at all.

In summing up the work reported the following conclusions may be drawn:

1. A properly prepared inoculant applied properly to the soil and keeping the soil in condition for the proper development of these organisms, will in most cases be beneficial from the standpoint of inoculation.

2. The indispensable conditions for successful application of the preparation are: a mellow soil, proper moisture content and well selected fertilizers.

3. With the precautions noted, soil inoculation may be practiced on a large scale under field conditions.

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PLATE 1

Fɪɢ. 1. A Typical Root of Vetch from a Plot, Fertilized with Minerals Without
Nitrates and Inoculated with Nodule Bacteria

Fɪɢ. 2. A Typical Root of Clover from a Plot, Fertilized with Minerals without
Nitrates and Inoculated with Nodule Bacteria
There were a great number of small nodules which the photograph does not show.

Fɪɢ. 3. A Typical Root of Vetch where Nitrates were Used; No Nodules Are Present
even though the Plots Were Well Inoculated

Fɪɢ. 4. A Typical Root of Clover, where Nitrates Were Used; No Nodules Are
Present, even though the Plots Were Well Inoculated

Fig. 1

Fig. 2

Fig. 3

Fig. 4

IS IT POSSIBLE TO MAKE A BACTERIAL SOIL PREPARATION FOR NON-LEGUME CROPS?

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Soon after the introduction of nitragin, attempts were made to work out also a bacterial soil-fertilizing preparation for non-legumes. At first, it was thought, that the nodule microbes could be utilized, but experiments showed that infection of the crops with *Bacillus radicicola* gave no results whatever. Neither soil inoculation, nor infection of the seeds, nor even injection of the nodule microbe cultures into the stems, had any influence on the crops.

The failure to utilize the nitrogen-fixing organisms for all crops induced the search for a preparation of cultures of other microbes. It was expected that these preparations would intensify the bacterial processes in the soil which in turn would have a beneficial influence on the development of the plants. The question at once arises as to whether any one ever attained an intensification of these processes with the methods of inoculation practiced? The first preparation "Alinit" was introduced by a German landowner named Caron on his estate Ellenbach. He prepared a culture of an organism which is at times very abundant in the soil; it was named *Bacillus ellenbachensis*. The biochemical or physiological characters were not investigated.

Caron (3) had not even identified the species of the microbe, some investigators identified it as *B. megatherium* [Stoklasa (17)], others as *B. subtilis* [Lauck (10)], Severin (16) found two microbes in Alinit which he named *B. ellenbachensis*. Hartleb (7) regards this microbe as an independent species of the hay bacillus group. The biochemical behavior of the Alinit organisms was investigated by Stutzer and Hartleb (18) and they place them in the group of typical putrifying or ammonia-producing organisms. Besides the above microbes some preparations carried also nitrifying organisms, like that of Beddies (2). Lipman (11) conducted experiments inoculating the soil with various species of Azotobacter, but there was no increase of nitrogen in the soil or plants.

These preparations were tested out and in most cases the results were negative. It will suffice to mention the work of Lutoslawski (12), West (20), Gerlach and Vogel (5) and Koch (9). It has been shown that the ammonifying and nitrifying organisms carried in those preparations are present in the soil and therefore such preparations are of no value as inoculants. Attention must, however, be directed to the non-symbiotic nitrogen-fixing bacteria, such as *Clostridium pasteurianum* and Azotobacter. Düggeli (4) realized the importance of such studies and investigated the effect of various substances on the nitrogen fixing organisms. It has been recognized that in some soils the nitrogen-fixing organisms are insufficiently

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[1] Translated from the Russian by Jacob S. Joffe, New Jersey Agricultural Experiment Stations.

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provided with carbonaceous matter. This impedes the process of nitrogen fixation, for the carbonaceous material is essential as a source of energy for these organisms. The store of soil nitrogen is thus more readily exhausted and the nitrogen problem becomes acute. In artificial cultures nitrogen fixation proceeds favorably when sugars, alcohols, calcium salts of organic substances, etc., are used. Under field conditions nearly all of these are absent from the soil. The question arises, what are the materials in the soil that are utilized as a source of energy by the nitrogen fixing organisms? Gerlach and Vogel (5) found that starch, cane sugar or mannitol were not used by the nitrogen fixing organisms and crop yields were depressed. Koch (9) attempted to explain the failure of Gerlach and Vogel. According to him the addition of the nutrients increases the microbial population in the soil to such an extent that they compete with the plants for food. The increase in crop yields should come in the second year, due to the decomposition of microbial bodies. He repeated the experiments and obtained an increase of yield amounting to nearly 250 per cent.

The source of carbon for the nitrogen fixing bacteria in the soil was not disclosed by these experiments, moreover the substances used in the experiments of Gerlach and Vogel could find no practical application. The investigations of Pringsheim (14) and Koch (9) seem to have solved the question. Three series of flasks were filled with a mineral solution for the nitrogen fixing bacteria; in the first series sugar was used as a source of carbon; in the second, mannitol; in the third, cellulose (Swedish filter paper). The first two series of flasks were inoculated with a pure culture of Azotobacter, the third with a mixture of aerobic cellulose bacteria and Azotobacter. After a certain period total nitrogen was determined by the Kjeldahl method. The results showed that the cultures inoculated with cellulose bacteria and Azotobacter gave the highest amount of nitrogen. It is known that the aerobic cellulose bacteria decompose cellulose, forming as intermediary products various organic acids. The calcium salts of these acids are a suitable source of carbon for the nitrogen-fixing bacteria. In the soil, great masses of vegetation are being decomposed by the cellulose bacteria, and the resulting products (organic salts of the alkali metals) may well serve as a source of carbon for the nitrogen-fixing bacteria. The above mentioned experiments also teach us the methods of microbiological operations for the stimulation of cellulose decomposition in soils rich in undecayed vegetative residues such as peat soil, soil after a good harvest of legumes, etc. One may expect, a priori, that the addition of cellulose bacteria and Azotobacter to such soils fertilized with mineral manures must exercise a favorable influence upon their fertility.

Makrinoff (13) has shown that the proper selection of mineral manures exerts a definite favorable influence on the legume bacteria. Such a selection must not only serve the needs of plants, but must also suit the physiological and biochemical peculiarities of the microbes used. The question arises: how should we fertilize a soil, rich in plant residues, when a mixture of cellulose bacteria and nitrogen fixing organisms is applied? The cellulose bacteria form, as intermediary products, organic acids whose calcium salts are utilized as sources of carbon for Azotobacter. For this reason the application of lime is an indispensable condition for success. Thomas slag, potassium salts, or

wood ashes are important. The first experiments were conducted on virgin peat soil; four plots were used, the first being the control plot; the other three received the following treatment:

> 250 poods[2] of lime per desiatina[3]
> 24 poods of Thomas slag per desiatina
> 24 poods of potassium salts per desiatina

The first two plots were not inoculated, the third plot was inoculated with nitrogen assimilating bacteria (Azotobacter), the fourth plot with a mixture of Azotobacter and aerobic cellulose bacteria as outlined by Van Iterson (19).

Cellulose bacteria could be cultivated in the following mineral solution:

		per cent
K_2HPO_4		0.5
$MgSO_4$		0.1
$(NH_4)MgPO_4$		2.0

To this solution 0.1 per cent of soil extract was added. The latter is made up as follows: a tzernozeme soil is treated with a 10-per cent HCl solution to remove various mineral substances; after 1 or 2 days digestion, the HCl is poured off, and the soil is washed with water until free from HCl. The soil is then digested with a 10-per cent ammonia solution for 1 or 2 days, the mixture being stirred frequently. The ammonia digest is poured off into a flat dish and evaporated on a steam bath. The residue is an ammoniacal salt of humic acid. The medium thus prepared was poured into "Kressling flasks." Filter paper made by Schleicher and Schühl was then added. Bacterial growth in the form of a yellow deposit appears at the surface after 24–48 hours. The filter paper becomes slimy and settles to the bottom. The yellow growth of the cellulose bacteria accumulates at the bottom and the filter paper dissolves rapidly. At that stage the cultures are rich in cellulose-destroying organisms, and Azotobacter is added. This preparation was used for sprinkling the seeds, oats having been used in the experiment.

The results of the experiment were as follows:

Plot 1. No crop could be harvested.
Plot 2. Crop weighed 16 pounds.[4]
Plot 3. Crop weighed 41 pounds, an increase of 156 per cent over plot 2.
Plot 4. Crop weighed 57 pounds, an increase of 257 per cent over plot 2.

Plate 1, figure 1 represents the standard sheaves from one square arshine[5] from plots 2, 3 and 4.

The second experiment, was conducted on a peat soil that had been under cultivation for a long time. The procedure followed was the same as in the

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[2] Pood = 16.38 kgm.
[3] Desiatina = 2.7 acres.
[4] A Russian pound is 0.41 kgm.
[5] An arshine is equivalent to about one meter.

preceding experiment. The size of the plots was 18 square arshines. Plate 1, figure 2 shows representative sheaves. The data are as follows:

Plot 1. Crop weighed 54 pounds.
Plot 2. Crop weighed 67 pounds, increase of 24 per cent over plot 1.
Plot 3. Crop weighed 74 pounds, increase of 10.5 per cent over plot 2.
Plot 4. Crop weighed 94 pounds, increase of 40.3 per cent over plot 2.

Thus the mineral manuring gave crop increase of 24 per cent. Bacterial infection with nitrogen-fixing bacteria brought about an improvement of the crop equally only 10.5 per cent (over plot 2); cellulose bacteria supplemented with nitrogen-fixing Azotobacter led to the greatest increase of the crop equalling 40.3 per cent.

The vegetation on plot 4, infected with cellulose and nitrogen-fixing microbes, was particularly dense and vigorous in comparison with that on the other three plots. Plots 2 and 3 differed little. The roots and stems on the infected plots 3 and 4 were better developed than on plots 1 and 2. The average lengths of stem at the time of harvest were:

	cm.		cm.
Plot 1	95	Plot 3	105
Plot 2	105	Plot 4	116

Plate 2 shows the roots and stems of representative plants on the different plots.

In these experiments only the crops from the three plots infected with Azotobacter attract our attention. It is usually assumed that Azotobacter is not capable of influencing the crops; nevertheless the third plot in the first experiment showed a crop increase over that of plot 2 of more than 150 per cent. This result may be explained by the presence of cellulose bacteria in the peat soil. This same plot in the second experiment showed only an insignificant increase. The difference may be explained by the differences in the composition and structure of the soil.

In the first experiment the soil was represented by a considerable depth of peat, the upper layer of which had a spongy structure; the second experiment was made on a cultivated soil acid in reaction and whose organic matter was in an advanced stage of decomposition. In this soil the cellulose bacteria had probably disappeared.

Similar experiments were made on the swampy experimental field of Novogord, at the Pechersky Agricultural Station and elsewhere. The arrangement and treatment of the plots were the same as in the preceding experiments. The plan and results are given in table 1.

The vetch shows an increase in yield; the clover also gave a visible increase; as for the oats there was a decrease.

In experiment 8 some effect of bacterial infection even where no lime was used was obtained thanks to the rather high proportion of lime in this black soil, which also has a limestone subsoil.

The above experiments were made in years 1915–16.   Only in 1917 a communication was received concerning the experiments of Bottomley (1) with "bacterized peat."   His experiments involved the mixing of ground peat with lime and Thomas slag, and infecting it with "humate" which probably means cellulose bacteria.   After two or three weeks he sterilized the peat with steam and infected it with Azotobacter.

TABLE 1

The influence of inoculation with cellulose and nitrogen fixing bacteria

PLANTS AND LOCALITY OF EXPERIMENT	FERTILIZERS USED PER DESIATINA*				YIELDS PER PLOT					
	Super-phos-phate	Thomas slag	K₂SO₄	CaO	Plot 1 (con-trol)	Plot 2 (minerals without inocula-tion)	Plot 3 (minerals and Azotobacter)		Plot 4 (Minerals, Azotobacter, and cellulose bacteria)	
							Yield	In-crease over plot 2	Yield	In-crease over plot 2
	poods†	*poods*	*poods*	*poods*	*pounds*‡	*pounds*	*pounds*	*per cent*	*pounds*	*per cent*
Novorgorod Experiment Station										
1. Vetch............	..	24	12	150	1.0	11.5	16.5	43.5	16.5	43.5
2. Clover...........	..	24	12	150	5.9	6.6	7.2	9.1	10.3	56.0
3. Timothy........	..	24	12	150	10.0	28.0	31.0	10.7	29.0	3.5
4. Oats............	..	24	12	150	4.2	4.2	4.2	0.0	2.8	....
5. Oats............	..	24	12§	200	There was more vigorous growth on the inoculated plots					
Pecherskaya Experiment Station										
6. Barley..........	..	31	24	150	....	7.5	10.5	40.0	10.25	36.6
7. Barley..........	20	..	24	150	....	9.75	8.9	....	17.9	83.6
Yeletz Experiment Station										
8. Oats...........	..	..	..	...	....	3.46	....	....	4.20	21.4

* Desiatina = 2.7 acres.
† Pood = 16.38 kgm.
‡ Russian pound = 0.41 kgm.
§ Wood ashes were used in place of potassium fertilizers.

These experiments have a certain analogy to the field experiments described here.

The proposed treatment of soils rich in organic residues, is based on the possible acceleration of decay of such inert and difficultly decomposable materials.   By this process it is possible to avoid carbonization and humification of soils rich in organic matter.

Hall (6) recommends mineral manuring with saltpeter, phosphorus and potassium for peat soil.   The above described method of manuring is more

advantageous inasmuch as the cellulose bacteria are effective in decomposing the organic residues, and besides, the nitrogen accumulation is important.

The above described experiments must be regarded as preliminary. The work is being continued on a large scale and the results will be published in the near future.

CONCLUSION

Bacterial inoculation and soil cultivation and fertilization must not only strictly correspond to the needs of plants, but also to the physiological requirements of the microbe employed.

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FIG. 2

Plot 2 Plot 3 Plot 4
FIG. 1
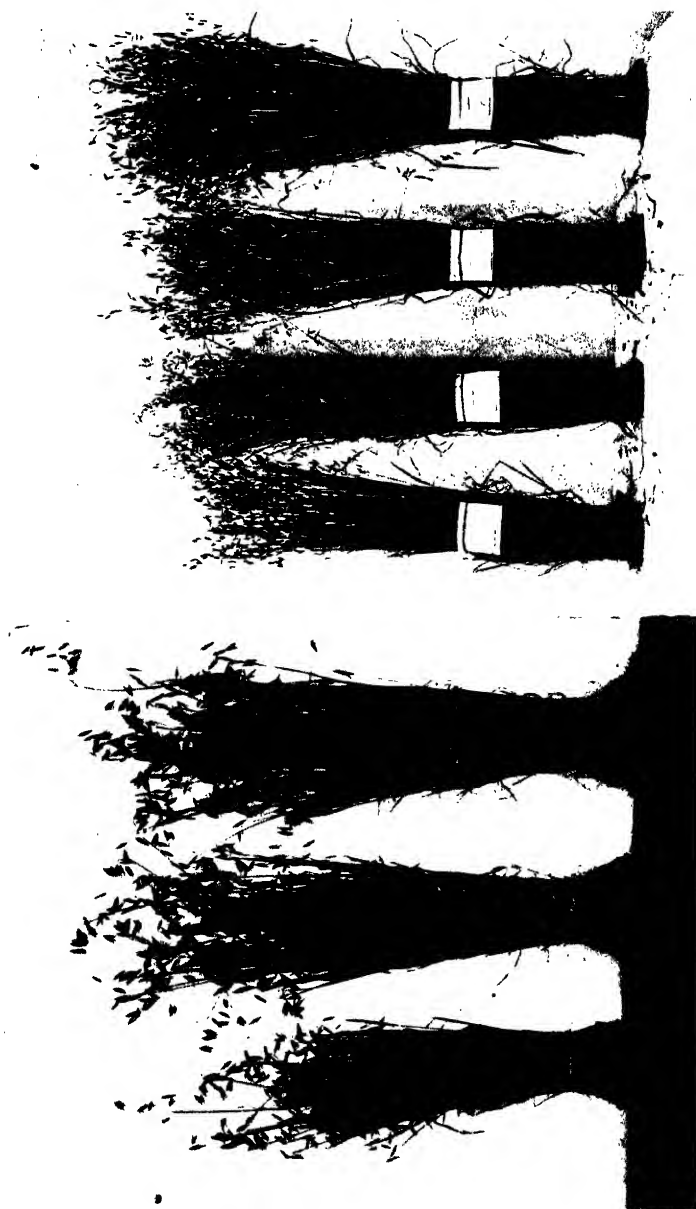
RELATIVE AVAILABILITY OF THE PHOSPHORUS OF RAW ROCK AND ACID PHOSPHATE IN SOILS

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INTRODUCTION

It is a mooted question among soil workers whether acid phosphate or rock phosphate is the better and the more economical source of phosphorus for crop production and the maintenance of soil fertility. Notwithstanding the great amount of work on this problem that has been done in various parts of the world, the question is far from being solved.

The results of investigations reported are often conflicting and sometimes not strictly comparable. It was thought advisable, therefore, to compare these two forms of phosphatic fertilizers in their behavior after they are applied to various types of soil, and also to study some of the factors that influence their behavior.

It would be of fundamental importance to know: What becomes of the phosphorus when phosphatic fertilizer is applied to the soil? What reactions take place? To what extent is phosphorus "available" when "water soluble" acid phosphate is incorporated with the moist soil mass?

As is generally known, one of the strongest claims of acid phosphate advocates is that acid phosphate is water soluble and that when it is applied to the soil, phosphorus becomes immediately available for the use of plants, while phosphorus in rock phosphate is so insoluble that its availability is too low for the immediate use of growing crops. The validity of this contention is often doubted, for it has been observed that the phosphorus of water soluble acid phosphate could not be extracted from the soil to which it was previously added. It is often argued, however, that although this phosphorus can not be extracted with water, it is absorbed or even adsorbed by the soil particles and loosely held thereby. This phosphorus, it is further claimed, is in such state that plant roots are able to extract it far more easily then the phosphorus of insoluble rock phosphate. The data presented in this paper will tend to show that this general contention is also of questionable validity; that the phosphorus of acid phosphate or even of double acid phosphate (superphosphate) after this material is applied to some agricultural soils, becomes very insoluble; and that its solubility is not to any extent greater than the solubility of phosphorus from rock phosphate added to the same soil, under the same conditions.

EXPERIMENTAL

The present investigation was carried out on many soil types, the soils in the majority of cases being obtained from Champaign county, Illinois. The phosphatic fertilizers used were three different rock phosphates, five slags, ground apatite, iron and aluminum phosphates, steamed bone meal and acid and double acid phosphates. The composition of these phosphatic fertilizers is presented in table 1.

The comparative work on different soils was carried out with Tennessee rock phosphate as a representative of insoluble rock phosphate, and with double acid phosphate as an easily soluble phosphatic fertilizer.

TABLE 1

Phosphorus content of phosphatic fertilizers used

FERTILIZER	PHOSPHORUS	AMOUNT OF MATERIAL CONTAINING 4 MGM. OF PHOSPHORUS
	per cent	*gm.*
Tennessee rock phosphate	13.8	0.0290
Double acid phosphate	19.94	0.0201
Slag A	8.40	0.0476
Slag B	9.30	0.0430
Slag C	5.79	0.0691
Slag D	6.61	0.0605
Birmingham slag	8.55	0.0468
Blue rock	13.05	0.0306
Florida soft rock	14.77	0.0271
Apatite	12.36	0.0324
Iron phosphate	16.36	0.0244
Aluminum phosphate	17.09	0.0234
Acid phosphate	9.54	0.0419
Steamed bone meal	14.81	0.0270

The general procedure of the experiment was as follows:

Twenty-five grams of mineral soil or 12.5 gm. of organic soil (peat) was placed in a 350-cc. glass bottle, thoroughly mixed with a given amount of fertilizing material, moistened with distilled water, and allowed to stand for seven days at room temperature. At the end of this period, this mixture was shaken with 250 cc. of 0.2 N nitric acid for three hours in a shaking machine. Then it was filtered on a dry filter paper. A 200-cc. aliquot of clear solution was taken for determination of phosphorus. The volumetric method of analysis was followed in this work. The tables show averages of two determinations.

It is often recommended that acids sufficiently stronger than one-fifth normal be used in studies of weak acid extractions so that after the soil bases are neutralized, the remaining acidity will be equal to one-fifth normal. Such an arrangement, of course, would give the phosphatic compounds in different soils the same chance for equal solubility. This procedure, however, introduces a very objectionable feature for the comparative study of different soils. The solvent would necessarily be different for nearly every soil, and the

results could hardly be comparable. It seems as though we should accept soils as such; accept the conditions under which any given soil has to function, and make our observations, preserving these conditions intact.

Suppose there are given two soils; one is abundantly supplied with carbonates, while the other is very deficient in them. The acids formed in the soils will be used largely to neutralize the carbonates in the first soil, and will be available as free acids in the second soil. Naturally there will be more phosphorus available for crops in the second soil than in the first. The field observations at various experiment stations show that soils excessively supplied with lime do not respond very well to the application of phosphates. This well known fact among soil workers seems to justify the procedure here adopted.

In time, the biological activities of these soils will also add to the modification of their soil solution, but this phase of the problem does not enter into the realm of the present study.

BEHAVIOR OF PHOSPHORUS APPLIED TO DIFFERENT SOILS

The work was done on soils of different geological and morphological formations. Prairie soils were represented by three samples of brown silt loam; two of black clay loam; one each of drab clay loam, brown gray silt loam on tight clay, and brown sandy loam. Timber soils were represented by one sample each of yellow gray silt loam on gravel, yellow silt loam eroded and yellow gray sandy loam. Terrace soils were represented by brown sandy loam. Mixed loam was used as a bottom land type formed along rivers. Deep peat was a representative of swamp lands.

In each soil type the soils of three different depths were used for the comparative tests with the phosphatic fertilizers: (a) the plowed layer of $6\frac{2}{3}$ inches in depth, (b) the layer from $6\frac{2}{3}$ to 20 inches, and (c) the layer from 20 to 40 inches. These strata will be designated as surface, subsurface and subsoil, respectively. The second and the third layers, of course, differ from the first one in their physical and chemical properties, and the descriptive name of soils for each layer is given here in order to facilitate interpretation of the data presented. All soils in this experiment were from stock samples, collected in 1915 in Champaign county for the soil survey analyses, air-dried and pulverized at the time. Since then, they were kept in 2-quart fruit jars. The soils of Champaign county are described in Illinois Agricultural Experiment Station Soil Report (1).

These fourteen soils of three layers each, or forty-two samples in all, were treated with either Tennessee rock phosphate or double acid phosphate in such amounts that in each case 4 mgm. of phosphorus were applied to 25 gm. of mineral soil and to 12.5 gm. of the first two layers of peat soil. The results presented in table 2 show the percent of applied phosphorus that was extracted with 0.2 N nitric acid. In each case the amount of phosphorus extracted from the untreated soil was subtracted from the amount of phosphorus ex-

TABLE 2

Phosphorus recovered from Tennessee rock phosphate and double acid phosphate

SAMPLE NO.*	SOIL SURVEY NUMBERS	SOIL DESCRIPTION BY LAYERS	RECOVERY OF PHOSPHORUS		DEVIATION		ALKALI REQUIRED PER 10 CC. EXTRACTED SOLUTION
			From rock phosphate	From double acid phosphate	+ or −	Squared	
			per cent	per cent			cc.

Prairie soils

		Brown silt loam:					
1	7729	Brown silt loam..................	45.5	48.3	−2.8	7.84	11.4
2	7730	Brown silt loam passing into yellow clayey silt......................	35.3	36.8	−1.5	2.25	11.4
3	7731	Yellow clayey silt with till.........	0.2	0.0	+0.2	0.04	0.2
		Brown silt loam:					
4	7741	Brown silt loam..................	55.2	61.5	−6.3	39.70	10.6
5	7742	Brown silt loam with some yellow..	47.7	47.7	0.0	...	10.7
6	7743	Yellow clayey silt with some brown..	43.5	44.2	−0.7	0.49	11.3
		Brown silt loam:					
7	7765	Brown silt loam..................	50.2	49.2	+1.0	1.00	11.3
8	7766	Brown silt loam with some yellow..	37.7	33.5	+4.2	17.64	11.2
9	7767	Yellow clayey silt, more silty with depth........................	42.5	41.5	+1.0	1.00	11.0
		Black clay loam:					
10	7840	Black clay loam to dark brown.....	66.3	65.8	+0.5	0.25	12.4
11	7841	Drab to black clay loam...........	66.0	64.5	+1.5	2.25	12.6
12	7842	Yellow to brownish yellow and drab clay............................	53.0	53.8	−0.8	0.64	11.9
		Black clay loam:					
13	7825	Black clay loam with some sand....	58.0	55.7	+2.3	5.29	12.2
14	7826	Black clay loam, some gravel and sand.........................	49.5	50.0	−0.5	0.25	12.1
15	7827	Drab to olive colored clayey silt....	45.3	43.5	+1.8	3.24	11.8
		Drab clay loam:					
16	7843	Drab clay loam, dark.............	60.0	59.0	+1.0	1.00	10.0
17	7844	Drab clay loam, lighter at 12 in.....	56.7	65.0	−8.3	68.90	10.2
18	7845	Drab silty clay, pebbles and lime...	18.0	27.2	−9.2	84.64	10.5
		Brown gray silt loam:					
19	7801	Brown gray silt loam on tight clay..	61.5	68.7	−7.2	51.84	9.3
20	7802	Gray silt loam....................	58.7	58.7	+0.0	.....	8.9
21	7803	Yellow to grayish clayey silt.......	37.5	37.0	+0.5	0.25	4.7
		Brown sandy loam:					
22	7849	Brown sandy loam...............	66.3	67.2	−0.9	0.81	9.8
23	7850	Brown sandy loam, some sand......	56.8	53.5	+3.3	10.89	10.1
24	7851	Yellow sand, some silt............	45.8	42.5	+3.3	10.89	4.2

* In each soil type the first sample represents surface layer of the soil; the second sample in order represents subsurface, and the third one represents subsoil.

TABLE 2—*Continued*

SAMPLE NO.	SOIL SURVEY NUMBERS	SOIL DESCRIPTION BY LAYERS	RECOVERY OF PHOSPHORUS		DEVIATION		ALKALI REQUIRED PER 10 CC. EXTRACTED SOLUTION
			From rock phosphate	From double acid phosphate	+ or –	Squared	
			per cent	*per cent*			*cc.*
		Timber soils					
		Yellow gray silt loam on gravel:					
25	7816	Yellow gray silt loam on gravel.....	54.7	49.2	+5.5	30.25	12.0
26	7817	Yellow silt loam.................	46.0	43.0	+3.0	9.00	11.9
27	7818	Yellow clayey silt, some gravel....	50.5	45.8	+4.7	22.09	11.8
		Yellow silt loam:					
28	7858	Yellow silt loam, brownish gravelly.	70.5	68.5	+2.0	4.00	10.6
29	7859	Yellow silt loam to yellow sandy loam.......................	63.8	66.8	–3.0	9.00	11.4
30	7860	Yellow silt to gravelly sandy silt....	62.3	62.0	+0.3	0.09	11.7
		Yellow-gray sandy loam:					
31	7855	Yellow gray sandy loam, some brown..........	73.0	73.5	–0.5	0.25	12.0
32	7856	Yellow sandy loam, some gray.....	68.8	73.2	–4.5	20.25	12.1
33	7857	Yellow sand, little silt	68.0	69.5	–1.5	2.25	12.1
		Terrace soils					
		Brown sandy loam:					
34	7852	Brown sandy loam................	65.7	64.2	+1.5	2.25	12.0
35	7853	Brown sandy loam, variable........	46.5	44.0	+2.5	6.25	12.1
36	7854	Yellow sand, some clayey sand....	34.8	34.0	+0.8	0.64	12.0
		River bottom soils					
		Brown mixed loam:					
37	7861	Brown mixed loam................	48.5	50.0	–1.5	2.25	9.90
38	7862	Brown mixed loam................	42.5	46.3	–3.8	14.44	10.50
39	7863	Yellowish brown loam, some sand...	54.8	54.0	+0.9	0.81	11.3
		Deep peat:					
40	7870	Black decomposed peat, shells......	102.0	101.0	+1.0	1.00	2.1
41	7871	Black peat......................	110.8	113.0	–2.2	4.84	7.0
42	7872	Black to brown peat, drab clay at 30 inches.....................	66.8	70.0	–3.2	10.24	8.8

Algebraic sum of deviations   –15.6   451

Mean deviation   – .371

Standard deviation $\sqrt{\dfrac{\Sigma d^2}{N} - m^2} = \sqrt{\dfrac{451}{42} - .138} = 3.256$

Z = ratio of mean deviation to standard deviation $\Big\} = \dfrac{-0.371}{3.256} = -0.114$

tracted from the treated soil. The results represent the net gain due to the treatment; it was assumed that the amount of soil phosphorus extracted from the treated soil is the same under these conditions as the amount of phosphorus extracted from the untreated soil.

An examination of the results in table 2 reveals a rather striking fact, namely, that the degree of recovery of phosphorus from nearly every soil studied is practically the same, regardless of the source of the phosphatic material. Water soluble acid phosphate, after it is incorporated into the soil mass and moistened, becomes soluble in 0.2 N nitric acid only to the same extent as the Tennessee rock phosphate. There are some relatively small differences in solubility in some individual cases. On the whole, however, these differences are very unimportant, as one can judge from the application of Student's method of bio-metric analysis (2). Using forty-two soil trials in which the mean deviation is only -0.371, and the standard deviation 3.256, we find that the ratio of the former to the latter, or Z, is only -0.114. This value is too small to be significant, since it is not given in Student's tables for the calculation of probability. The smallest value of Z used in his tables is 1, and such value gives chances from 10 to 12 times as small as those considered at all significant.

Different soil types allow the recovery of different amounts of phosphorus. In this respect, the variations are very great. Thus, the soil of the third layer of the samples of brown silt loam (sample 3, table 2) did not allow any re-recovery; while, in the surface layer of peat, the recovery was complete. Indeed, the amount of phosphorus recovered from peat of the second layer was greater than the amount applied. The differences in phosphorus recovery are from 11 to 13 per cent, and seem to be larger than those which could be ascribed to the experimental error. In the majority of cases, the recovery of phosphorus varied between 40 and 60 per cent. On the whole, the recovery was somewhat greater in the surface layer than in the subsurface. The third layer, or the subsoil, gave the smallest recovery of phosphorus in all cases.

In order to ascertain whether or not other phosphatic fertilizers would follow the same general mode of behavior as observed with the Tennessee rock phosphate and double acid phosphate, the experiment was repeated on another sample of brown silt loam, using various phosphatic fertilizers. As one notices from table 1, these phosphorus-carrying substances varied in their phosphorus content very considerably. The amount of each substance used, however, was in every case equivalent to 4 mgm. phosphorus, as calculated from their analyses. Twenty-five grams of soil was used in every case. The amounts of phosphorus extracted with 0.2 N nitric acid, as well as the per cent of phosphorus recovery are given in table 3. The results show that, with the exception of iron phosphate and two or three brands of slag, the per cent of recovery is practically the same for the various phosphatic carriers. Acid phosphate gave no larger recovery than the majority of the so-called insoluble phosphatic fertilizers. These figures are rather interesting, espe-

TABLE 3

*Recovery of phosphorus from different phosphatic fertilizers applied to brown silt loam**

FERTILIZER	PHOSPHORUS EXTRACTED	PHOSPHORUS EXTRACTED	ALKALI REQUIRED PER 10 CC. OF EXTRACTED SOLUTION
	mgm.	*per cent*	*cc.*
Tennessee rock phosphate	2.35	58.8	11.6
Slag A	2.12	53.0	11.4
Slag B	2.11	52.8	11.4
Slag C	2.16	54.0	11.4
Slag D	2.33	58.3	11.4
Birmingham slag	2.23	55.8	11.5
Blue rock	2.28	57.0	11.6
Florida soft rock	2.37	59.3	11.6
Apatite	2.40	60.0	11.6
Iron phosphate	1.91	47.8	11.7
Aluminum phosphate	2.32	58.0	11.6
Acid phosphate	2.29	57.3	11.6
Steamed bone meal	2.15	53.8	. 11.6
Soil, alone			11.7
Acid, alone			12.7†

* In each case 4 mgm. of phosphorus were applied per 25 gm. of soil.

† 10 cc. of distilled water was used to wet the soil after fertilizer was added to it. In order to make the results comparable, 10 cc. of water was added to 250 cc. of acid before titration.

TABLE 4

*Phosphorus extracted with distilled water and with 0.2 N nitric acid from different phosphatic fertilizers**

FERTILIZER	WATER SOLUBLE PHOSPHORUS EXTRACTED		PHOSPHORUS SOLUBLE IN 0.2N HNO₃ AND EXTRACTED		ALKALI REQUIRED PER 10 CC. EXTRACTED SOLUTION
	mgm.	*per cent*	*mgm.*	*per cent*	*cc.*
Tennessee rock phosphate	0.08	2.0	3.94	98.6	13.0
Double acid phosphate	3.60	90.0	4.19	105.0	13.0
Slag A	0.00	0.0	3.89	97.3	12.9
Slag B	0.03	0.8	3.98	99.5	12.9
Slag C	0.23	5.8	4.05	101.0	12.8
Slag D	0.06	1.5	4.02	100.5	12.8
Birmingham slag	0.09	2.3	3.96	99.0	12.9
Blue rock	0.16	4.0	4.02	100.0	13.1
Florida soft rock	0.09	2.3	3.98	99.5	13.0
Apatite	0.01	0.3	4.08	102.0	13.0
Iron phosphate	0.15	3.8	3.72	93.0	13.1
Aluminum phosphate	0.22	5.5	4.07	101.8	13.1
Acid phosphate	3.40	85.0	3.88	97.0	13.1
Steamed bone meal	0.20	·5.0	4.01	100.2	13.0
Acid alone					13.1

* Two hundred and fifty cubic centimeters of either acid or water were used on fertilizer which contained ♦ mgm. of phosphorus per sample.

cially if one considers them in parallel with the data presented in table 4 which gives the amount and the per cent of phosphorus recovery from the same amount of fertilizing material alone (without the soil), when the extraction was made either with distilled water, or with fifth normal nitric acid.

The data in table 4 show that the phosphorus in acid phosphate is recovered with distilled water to the extent of 85 per cent, and from double acid phosphate to the extent of 90 per cent. None of the other phosphates had a solubility in water amounting to six per cent, and some of them, as apatite and one of the slags, were extremely insoluble in water.

When the same materials were extracted with 0.2 N nitric acid, under the same conditions, i.e., without mixing them with the soil, the per cent of recovery was about 100 in nearly every case (See table 4).

It is evident that there is something in the soil that prevented this phosphorus recovery. Undoubtedly some of the acid, after it is added to the soil, reacts with some of the soil bases, forming nitrates. This would be especially true if carbonates of calcium and magnesium are present. Such a reaction would decrease the concentration of the acid, and thus cause the decrease in the amount of phosphorus extracted. Anticipating such action in some soils that are more or less supplied with carbonates, an aliquot of clear extracted solution was taken and titrated against a standard alkali (0.1484 normal), using methyl-red-para-nitro-phenol for the indicator. The figures for relative titrations are given in tables 2, 3 and 4 (last column). They show that fertilizing materials alone do not reduce the concentration of nitric acid to any appreciable extent (table 4). The fertilizing materials after they are applied to brown silt loam, as recorded in table 3, reduce the acid concentration rather uniformly to about 90 per cent of its original strength. This in no way accounts for the reduction of phosphorus recovery to about 50 or 60 per cent of its recovery from the fertilizing materials themselves. The titrations recorded in table 2 explain the failure of phosphorus recovery in only a very limited number of cases. Sample 3, or the subsoil layer of brown silt loam, contained a large amount of carbonates, which used practically all the acid present, thus making the phosphorus extraction impossible. Perhaps samples 21 and 24 also behaved in a similar way. With these three exceptions, however, the reduction in the acid concentration fails entirely to explain the behavior of phosphorus in all these soils. The lack of correlation between acid concentration and the ultimate phosphorus recovery is very apparent, if one compares the surface soil with its subsurface and subsoil layers in regard to the phosphorus extraction and the concentration of nitric acid at the end of the extraction. Peat, represented by samples 40, 41, and 42, affords an interesting observation. The carbonates of the surface layer reduce the acid concentration to about one-sixth of its original strength. In spite of that, the phosphorus recovery was practically complete. In the subsoil layer, sample 42, the acid concentration was over four times as great as in the surface layer, yet the phosphorus recovery was reduced to 70 per

cent. Again, with the acid in the subsurface layer, sample 41, slightly weaker than that in the subsoil layer, the recovery was complete. There was even some stimulating effect noticed on the soil phosphorus.

Very little or no correlation can be traced if one compares, in this respect, the surface, subsurface or the subsoil layers among themselves. Noticing the fact that the subsoil layer of the peat soil contains a considerable amount of clay particles or mineral matter, the suggestion arises that the mineral portion of the soil forces phosphorus to react in the way here observed. It would seem probable that some double salts of phosphorus with iron or aluminum, or with both, are formed that are less soluble than the simple phosphates of calcium, iron and aluminum. The presence of silica in the form of silicic acid perhaps has considerable influence on the formation of these complex combinations. However, the presence of bases commonly found in the soil is evidently essential for their formation. The silica of quartz sand, which was rather coarse in texture, prevented some phosphorus recovery, as may be noted in figure 3. In this figure, data of another experiment are shown where different amounts of phosphorus were added to 25 gm. of quartz sand, and later extracted with 0.2 N nitric acid.

TABLE 5

*Recovery of phosphorus from 25 gm. of brown silt loam and yellow-gray silt loam**

	First		Second	Third	Fourth	Fifth	Total	
	mgm.	*per cent*	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*per cent*
Brown silt loam:								
With rock phosphate.........	1.86	46.5	0.47	0.24	0.13	0.09	2.79	69.8
With double acid phosphate..	1.75	43.8	0.46	0.21	0.12	0.02	2.56	64.0
Yellow-gray silt loam:								
With rock phosphate.........	3.02	75.5	0.25	0.09	0.02	0	3.38	84.5
With double acid phosphate..	3.10	77.5	0.24	0.10	0.05	0.01	3.50	87.5

(Header spanning: "PHOSPHORUS EXTRACTED")

* Treated with 4 mgm. of phosphorus of either Tennessee rock phosphate or double acid phosphate. Five consecutive extractions were made with fifth normal nitric acid.

At this point, it is desirable to emphasize the fact that the phosphorus, which 0.2 N nitric acid fails to extract from a given soil, exists in the soil in such a complex combination that even subsequent extractions with fresh nitric acid of the same strength fail to bring the phosphorus into solution. Separate portions of two soils, brown silt loam and yellow gray silt loam, were treated with Tennessee rock phosphate and double acid phosphate. The extractions with nitric acid were filtered and the residues washed four times with warm distilled water. The residue was treated with fresh nitric acid, and the procedure was repeated five times. The results are presented in table 5, and show that but a relatively small amount of phosphorus was extracted from those soils after the first extraction, and the amount decreased with every subsequent extraction.

FACTORS MODIFYING THE PHOSPHORUS RECOVERY FROM SOILS

The factors that may modify the behavior of phosphorus in soil are (a) time of reaction, (b) temperature during the reaction, (c) moisture content of soil, (d) amount of fertilizer applied, and (e) chemical nature of various substances that are used in agricultural practice or are present in soils in different amounts.
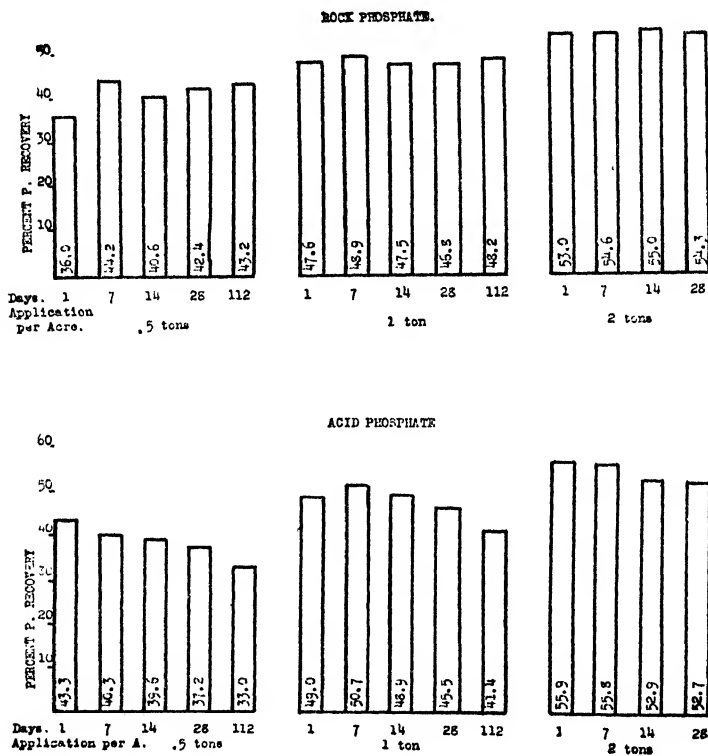
FIG. 1. EFFECT OF TIME OF REACTION AND THE AMOUNT OF PHOSPHORUS PRESENT ON THE PER CENT OF PHOSPHORUS RECOVERY FROM BROWN SILT LOAM

The phosphorus was added to the soil in the form of either rock or acid phosphate; 0.2 N HNO_3 was used for extraction.

Time of Reaction

In most of the chemical reactions, time is a very important factor. In order to determine the extent of its importance in reactions between soluble acid phosphate and the soil bases, the influence of time was studied with two soils and with quartz sand. The experiments were arranged in such a way that the influence of amounts of fertilizers present for reaction was also studied

at the same time.   Twenty-five gram portions of soil were treated with 0.0125 gm., 0.025 gm. and 0.0500 gm. of Tennessee rock phosphate and double acid phosphate, the amounts being equivalent to 1000, 2000 and 4000 pounds of fertilizer per acre (2,000,000 pounds of soil), respectively.   Complete sets of the treated soils, moistened with distilled water, were left for various lengths of time, after which the extractions with 0.2 N nitric acid were made and the phosphorus determined.

ROCK PHOSPHATE

PERCENT P. RECOVERY

Days.	1	7	14	91	1	7	14	91	1	7	14	91
	11.7	23.8	20.9	26.3	20.8	24.3	23.1	31.3	25.3	29.1	31.2	31.3

Application per Acre   .5 ton   1 ton   2 tons

ACID PHOSPHATE

PERCENT P. RECOVERY

Days	1	7	14	91	1	7	14	91	1	7	14	91
	20.3	24.4	17.5	24.4	25.5	26.5	25.3	28.1	26.7	32.5	32.1	33.9

Application per Acre   .5 ton   1 ton   2 tons
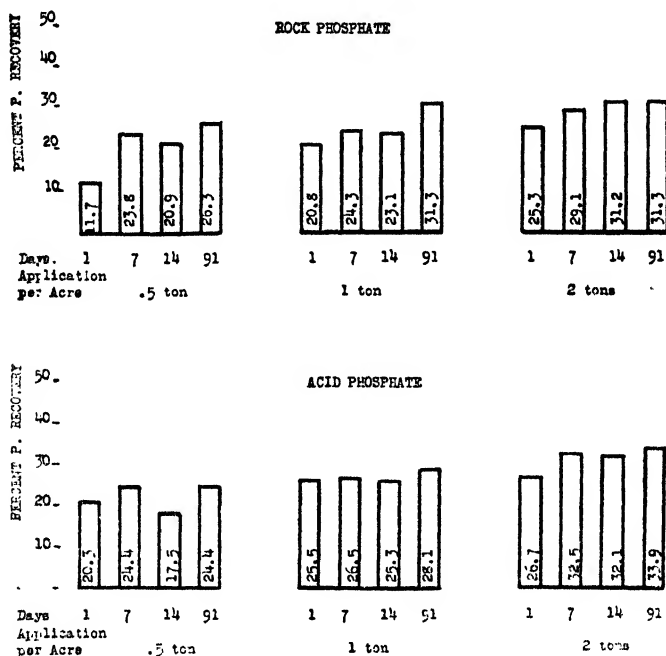
FIG. 2. EFFECT OF TIME OF REACTION AND THE AMOUNT OF PHOSPHORUS PRESENT ON THE PER CENT OF PHOSPHORUS RECOVERY FROM BLACK CLAY LOAM

The phosphorus was added in the form of either rock or acid phosphate; 0.2 N HNO$_3$ was used for extraction.

The results are presented in figures 1, 2 and 3, and they show that, in a general way, the reaction is complete in one day.   In brown silt loam, treated with double acid phosphate, the phosphorus recovery is slightly, but consistently, decreased with the increase in the time allowed for the reactions. This tendency was not observed in black clay loam or in quartz sand.   The greatest recovery in every case was obtained in quartz sand, and the smallest in black clay loam, the brown silt loam occupying the intermediate position.

Moisture content

In all the experiments recorded here, optimum moisture content (between 50 and 70 per cent of saturation) was maintained in soils treated with phosphatic fertilizers. This factor, as one notices in figure 4, is not as essential
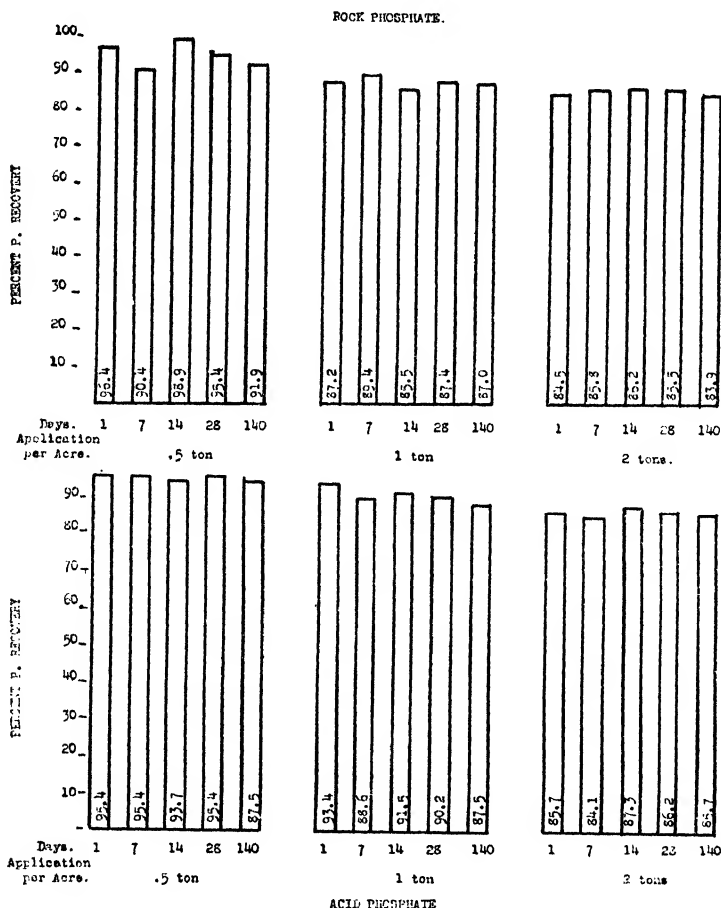
Fig. 3. Effect of Time of Reaction and the Amount of Phosphorus Present on Per Cent of Phosphorus Recovery from Quartz Sand

The phosphorus was added in the form of either rock or double acid phosphate; 0.2 N HNO$_3$ was used for extraction.

as might be expected. The reaction appears to take place after nitric acid is applied for the extraction, proceeds in rather strongly acid solutions, and is completed during the three hours of shaking in the shaking machine.

In several lots of brown silt loam, increasing moisture contents were maintained at from 10 to 100 per cent of saturation. The phosphorus recovery was practically the same in all trials with rock phosphate, and within 6 per cent in the case of double acid phosphate.
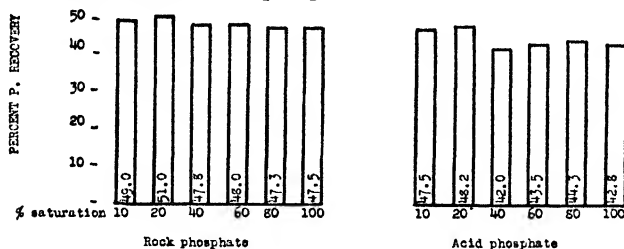
FIG. 4. EFFECT OF MOISTURE CONTENT IN BROWN SILT LOAM ON THE PER CENT OF PHOSPHORUS RECOVERY FROM 25 MGM. OF THIS SOIL, TREATED WITH 4 MGM. OF PHOSPHORUS IN EITHER ROCK PHOSPHATE OR IN DOUBLE ACID PHOSPHATE; 0.2 N HNO$_3$ WAS USED FOR EXTRACTION
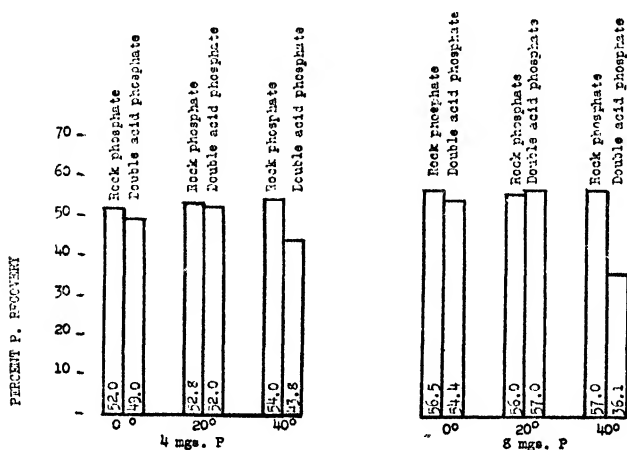
FIG. 5. EFFECT OF TEMPERATURE ON THE AMOUNT OF PHOSPHORUS EXTRACTED FROM 25 GM. OF BROWN SILT LOAM, TREATED WITH 4 OR 8 MGM. OF PHOSPHORUS IN THE FORM OF EITHER ROCK OR ACID PHOSPHATE

The degrees indicate the temperature at which soils, treated with phosphatic fertilizers, were kept for 7 days before extraction. Data represent per cent of phosphorus recovery with 0.2 N HNO$_3$.

Temperature

The temperature at which reaction takes place was studied with brown silt loam soil, which was kept at 0°, 20°, and 40°C. As one notices in figure 5, at all three temperatures, the recovery of phosphorus from rock-phosphate-treated soil was practically the same. This holds true whether 4 or 8 mgm.

of phosphorus were originally applied. Double acid phosphate offers the same recovery of phosphorus at two of the temperatures studied; namely, at 0° and 20°C. At 40°C., however, the phosphorus recovery does not follow the general tendency. In the application amounting to 4 mgm. of phosphorus the recovery was about 10 per cent less than from soils with rock phosphate, while in the 8 mgm. application the difference was over 20 per cent. It would seem, therefore, that at a higher temperature, the reaction of water soluble double acid phosphate was carried to completion more rapidly than at a lower temperature, and that the newly formed phosphatic compound or compounds are more insoluble than those formed at a lower temperature.

Effect of various substances on recovery of phosphorus

It is reasonable to suppose that different chemical substances would modify the mode of reaction of soluble phosphatic compounds with soil, as well as to modify the character of the resultant soil solution. Two different soils, brown silt loam and yellow gray silt loam, a prairie and a timber soil, respectively, were treated with various substances which are often used in farm practice. The soils later were treated with Tennessee rock and with double acid phosphate and phosphorus was extracted and determined in the usual way. For comparison, quartz sand was treated in the same way. The substances used in this experiment included CaO, $CaCO_3$, KCl, $NaNO_3$, $(NH_4)_2SO_4$, and $CaSO_4$ in amounts of 0.1 gm. of substances per 25 gm. of yellow gray silt loam or quartz sand, and 0.05 gm. for the same amount of brown silt loam.

The results summarized in tables 6, 7 and 8 show that, in the amounts here used, KCl and $NaNO_3$ did not influence to any appreciable extent the recovery of phosphorus either from rock or double acid phosphate treated soils. CaO and $CaCO_3$ were also without any effect on yellow gray silt loam or sand, while they caused some depression in phosphorus recovery in brown silt loam.

Both of the above mentioned sulfates, on the other hand, caused a considerable increase in the phosphorus recovery from both agricultural soils. The recovery was somewhat larger from soils treated with the easily soluble phosphatic fertilizer than from those treated with rock phosphate.

In the case of quartz sand, treated with rock phosphate, the recovery was not affected, while a little increase was observed in sand treated with double acid phosphate. The increase in the latter case could hardly be called significant, while the increase in phosphorus recovery from the agricultural soils is too great to be attributed to experimental error.

If these results are reliable, they may throw some light on the question of the effect of application of gypsum to soils. The low phosphorus content is a limiting factor in a great many agricultural soils. The application of gypsum to some of these soils causes an increase in crop production. It would seem that, by modifying the character of the soil solution, gypsum indirectly causes a greater availability of phosphorus to plants. This would

TABLE 6

Effect of various substances on the amount of phosphorus extracted with 0.2 N HNO₃ from brown silt loam*

| | | PHOSPHORUS EXTRACTED | |
		After subtracting blank	Increase over soil treated with phosphorus only
		mgm.	*per cent*
Rock phosphate alone...........................		1.85	
Rock phosphate	+CaO............................	1.72	−7.0
	+CaCO₃...........................	1.73	−6.5
	+KCl............................	1.84	−0.5
	+NaNO₃..........................	1.84	−0.5
	+ (NH₄)₂SO₄......................	2.12	14.6
	+CaSO₄..........................	2.16	16.8
Acid phosphate alone............................		1.59	
Acid phosphate	+CaO............................	1.57	−1.3
	+CaCO₃...........................	1.63	2.5
	+KCl............................	1.67	5.0
	+NaNO₃..........................	1.66	3.8
	+(NH₄)₂SO₄...:..................	2.03	27.7
	+CaSO₄..........................	2.01	26.4

* Treated with either rock or acid phosphate that contained 4 mgm. of phosphorus. Amount of CaO or salt used = 0.05 gm. per 25 gm. of soil.

TABLE 7

Effect of various substances on the amount of phosphorus extracted with 0.2 N HNO₃ from 25 gm. of yellow-gray silt loam*

| | | PHOSPHORUS RECOVERY | |
		After subtracting blank	Increase over soil treated with phosphorus only
		mgm.	*per cent*
Rock phosphate alone...........................		2.79	
Rock phosphate	+CaO............................	2.77	0
	+CaCO₃...........................	2.74	−2
	+KCl............................	2.79	0
	+NaNO₃..........................	2.77	0
	+(NH₄)₂SO₄.....................	3.31	19
	+CaSO₄..........................	3.28	18
Acid phosphate alone............................		2.78	
Acid phosphate	+CaO............................	2.87	3
	+CaCO₃...........................	2.83	2
	+KCl............................	2.89	4
	+NaNO₃..........................	2.81	1
	+(NH₄)₂SO₄......................	3.48	25
	+CaSO₄..........................	3.46	24

* Treated with 4 mgm. phosphorus in the form of either rock or acid phosphate. Amount of CaO or salt used = 0.1 gm.

TABLE 8

*Effect of various substances on the amount of phosphorus extracted with 0.2 N HNO₃ from 25 gm. quartz sand**

		PHOSPHORUS RECOVERY	
		After subtracting blank	Increase over soil treated with phosphorus only
		mgm.	*per cent*
Rock phosphate alone..........................		3.44	
Rock phosphate	CaO..........................	3.45	0
	+CaCO₃........................	3.42	−1
	+KCl..........................	3.37	−2
	+NaNO₃........................	3.29	−4
	+(NH₄)₂SO₄....................	3.43	−1
	+CaSO₄........................	3.52	2
Acid phosphate alone..........................		3.43	
Acid phosphate	+CaO..........................	3.53	2
	+CaCO₃........................	3.42	−2
	+KCl..........................	3.42	−2
	+NaNO₃........................	3.52	1
	+(NH₄)₂SO₄....................	3.72	7
	+CaSO₄........................	3.69	6

* Treated with either rock or acid phosphate that contained 4 mgm. phosphorus. Amount of CaO or salt used = 0.1 gm.

TABLE 9

*Effect of calcium carbonate upon recovery of phosphorus from 25 gm. brown silt loam**

	PHOSPHORUS IN EXTRACT	PHOSPHORUS IN EXTRACT DUE TO TREATMENT	PHOSPHORUS RECOVERY
	mgm.	*mgm.*	*per cent*
Soil alone..	0.31		
Soil + rock phosphate............................	2.01	1.70	42.5
Soil + rock phosphate + 1 gm. CaCO₃..............	1.04	0.73	18.3
Soil + rock phosphate + 2 gm. CaCO₃..............	0.12	−0.19	−4.8
Soil + rock phosphate + 4 gm. CaCO₃..............	0.00	−0.31	−7.8
Soil + double acid phosphate.....................	1.94	1.63	40.8
Soil + double acid phosphate + 1 gm. CaCO₃.......	0.99	0.68	17.0
Soil + double acid phosphate + 2 gm. CaCO₃.......	0.12	−0.19	−4.8
Soil + double acid phosphate + 4 gm. CaCO₃.......	0.06	−0.25	−6.3

* Treated with 4 mgm. of phosphorus of either Tennessee rock phosphate or double acid phosphate. 0 2 N HNO₃ was used for extraction.

explain in part the beneficial effect of gypsum on soils depleted in productivity. Evidently, a similar line of reasoning could be applied to ammonium sulfate, though this salt also supplies nitrogen, the soil content of which may also be a limiting factor in crop production.

It was noticed that lime and calcium carbonate, when used in small amounts, do not cause any decrease in the phosphorus recovery. It is sometimes observed in plot work or actual field practice that excessive amounts of limestone in soil inhibit the use of phosphorus by crops. To study this question in the light of the method of testing used in the present study, brown silt loam was treated with 1, 2, and 4 gm. of $CaCO_3$ per 25 gm. of soil. Afterwards this soil was treated with 4 mgm. of phosphorus in the form of either rock or double acid phosphate, moistened, allowed to stand, and then phosphorus was extracted as usual. Table 9 shows the results of this experiment. The phosphorus recovery in Brown silt loam, treated with the two phosphatic fertilizers, is practically the same, the figures being 40.8 and 42.5 per cent. One gram of $CaCO_3$ per 25 gm. of soil reduces this recovery to only 17 and 18.3 per cent. Two grams of $CaCO_3$ does not allow any recovery of phosphorus. Indeed, the total amount of phosphorus extracted is less than from the soil not treated with the phosphatic fertilizer. Evidently, even the extraction of soil phosphorus is inhibited. In the case of soil treated with 4 mgm. of $CaCO_3$ this inhibitive effect is still more pronounced. In one case only a trace of phosphorus was found.

The results obtained in this experiment could be anticipated on the ground that most, if not all, of the acid was neutralized by limestone, thus causing the phosphorus extraction to be effected by a neutral salt solution, whose power for solution of phosphatic compounds is naturally very low. The observed phenomenon is somewhat comparable to that observed in actual farm practice. Limestone present in soil in excessive amounts may neutralize the acid soils so completely and so quickly after they have been formed that phosphorus in the resultant neutral or even alkaline medium could not go into solution fast enough for the need of rapidly growing crops.

CONCLUSIONS

The results of these experiments seem to justify the following general conclusions:

1. After phosphorus in the form of phosphatic fertilizers is applied to ordinary mineral soils, it becomes considerably less soluble in 0.2 N nitric acid.

2. Peat soil is an exception in that it does not depress the recovery of phosphorus under the same conditions.

3. After phosphatic fertilizers are applied to the soil, the recovery of phosphorus from soil treated with double acid phosphate is no greater than the recovery of phosphorus from the same soil treated with ground rock phosphate, using 0.2 N nitric acid for the solvent in each case.

4. After the first extraction with 0.2 N nitric acid, the subsequent extractions with fresh acid fail to extract a considerable amount of additional phosphorus. Five consecutive extractions fail to recover the entire amount of phosphorus applied either in the form of rock phosphate or of double acid phosphate.

5. The reaction between the phosphorus of phosphatic fertilizers and the substances present in the soil proceeds very rapidly, the reaction being practically completed in these experiments the first day.

6. The moisture content of soil treated with the phosphatic fertilizer is not a factor in modifying the phosphorus recovery by 0.2 N nitric acid extraction.

7. High temperature (40°C. in comparison with 20°C.) may decrease the availability of phosphorus in acid phosphate treated soil, while it has no influence on rock phosphate. Phosphorus recovery is practically the same at temperatures of 0° and 20°C.

8. Of the various supplementary substances used (0.05 −0.10 gm. per 25 gm. of soil), CaO, $CaCO_3$, KCl and $NaNO_3$ do not materially affect the phosphorus recovery from rock or acid phosphate treated soils. This is in direct contrast with $(NH_4)_2SO_4$ and $CaSO_4$ which increase the phosphorus recovery very considerably, $(NH_4)_2SO_4$ causing an increase of 14.6 to 27.7 per cent, and $CaSO_4$ of 16.8 to 26.4 per cent. The latter case may explain in part the beneficial effect of gypsum application to some agricultural soils.

. 9. Calcium carbonate, in large amounts, inhibits phosphorus recovery, the effect being very much in proportion to the amount of limestone present in the soil. This finding is in agreement with observations that are sometimes made in farm practice.

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OXIDATION OF AMMONIA AND NITRITES BY MICROÖRGANISMS UNDER DIFFERENT CONDITIONS[1]

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Investigators have long realized that for vigorous nitrification both in the field and in the laboratory proper conditions of aeration and reaction of medium must be present.

As early as 1877 (12) when the study of nitrification was still in its pioneer stage, Schloesing and Müntz observed that for strong nitrate production an abundant supply of air is necessary. They wrote two years later (13) that the access to oxygen is an essential condition for vigorous nitrification. Schloesing (11) determined the amount of oxygen necessary to oxidize ammonia to nitrate and found a definite ratio. Winogradsky (14) writing on the oxidation of NH_3 in pure cultures makes the statement that the favorable influence of a more perfect aeration (in liquid cultures) is very marked. In 1903 Boullanger and Massol (4) incubated their cultures in Erlenmeyer flasks containing slag (scories cassés en petite morceaux) broken into small pieces, thus increasing the surface of their liquid cultures. They shook the flasks three or four times every day. Rapid nitrification was observed. Müntz and Laine (10) worked out an arrangement based on the same principle as above with the exception that they used bone black and peat instead of "scories." of Boullanger and Massol with the result that they obtained intensified nitrification. Barthel (1) claimed that by his aeration method a strong nitrification took place. The use of large bottomed shallow vessels has found favor with many investigators. Löhnis and Green (6) obtained maximum oxidation when the ratio between the depth and surface of the layer of culture medium was 1 to 90. Meyerhof (9) very considerably accelerated nitrification by the simple means of passing air through his culture media. Bonazzi (2) obtained greater intensity in nitrification by exposing larger surface and by constantly changing the surface exposed to air. He does not, however, think that increased availability of air to the culture had anything to do with the increase in nitrification. Boullanger (3) followed the work he had done with Massol in 1903. This time he used peat and carried out the experiment on a larger scale to see if production of nitrates by biological process could be put on a commercial basis. He let a solution of $(NH_4)_2SO_4$ flow through several cubic meters of peat inoculated with the nitrifying organisms. The amount of liquid passed through the peat daily was 200 liters containing 7.5 gm. $(NH_4)_2SO_4$ per liter. He obtained in the solution at the exhaust 138.2 gm. of calcium nitrate per liter.

EXPERIMENTAL

In the preliminary work of isolation of the nitrifying organisms which has been described elsewhere it was found that the oxidation of $(NH_4)_2SO_4$ in 25

cc. of nutrient solution containing 0.1 per cent of this salt took at the least 9
to 10 days even though 1 cc. of inoculum was used.   To increase the rate of
oxidation the following experiment was carried out.

Oxidation of Sodium Nitrite

One-pint milk bottles were fitted with double-holed rubber stoppers through
which were passed glass tubes bent at right angles, one of them reaching the
bottom of the bottles.   They were sterilized and into each was put 200 cc. of
a sterile solution which contains:

$NaNO_2$...:...1.0 gm.
Na_2CO_3...1.0 gm.
K_2HPO_4...0.5 gm.
NaCl..0.5 gm.
$MgSO_4$...0.3 gm.
$Fe_2(SO_4)_3$...trace
Water (conductivity)..1000 cc.

These solutions were inoculated with a culture of nitrate former which had
gone through a number of subcultures.   Sterile moist air was drawn through
the solution.   The determination of nitrates was made by the phenol-di-
sulfonic acid method and the hydrogen-ion concentration by the "color
standards" of Medalia (7); advance information of the material published later
by Medalia (8) was also used.

As will be seen from table 1 it took one week by this method of aeration for
the complete oxidation of the nitrite solution, whereas without aeration it
usually took more than one week to oxidize 25 cc. of the same medium.   The
rate of oxidation with aeration was 28.6 mgm. $NaNO_2$ per day.   The experi-
ment was repeated with the results recorded ("second test").   Oxidation
during the period of the experiment took place at the maximum rate of 31.4
mgm. of $NaNO_2$ per day.

Oxidation of $(NH_4)_2SO_4$

The apparatus used for the oxidation of $(NH_4)_2SO_4$ was the same as that used
for the oxidation of $NaNO_2$.   A solution containing the following nutrients
was used:

$(NH_4)_2SO_4$...1.0 gm.
K_2HPO_4...1.0 gm.
NaCl..2.0 gm.
$MgSO_4$...0.5 gm.
$Fe_2(SO_4)_3$...trace
Water (conductivity)..1000 cc.

Two hundred cubic centimeters of the sterile solution was placed in sterile
pint bottles and inoculated with a liquid culture of nitrite former.   Moist

sterile air was drawn through the solution. The nitrites were determined by the colorimetric method using sulfanilic acid and alpha-naphthylamin hydrochloride in acetic acid.

The results reported in table 2 were at first difficult to understand. The activity of the organism as indicated by the production of NO_2 was very slow.

TABLE 1

The oxidation of sodium nitrite

DATE	NaNO₂* OXIDIZED TO NITRATE IN TRIPLICATE SAMPLES			REACTION		
	1	2	3	1	2	3
	mgm.	mgm.	mgm.	pH	pH	pH
First test						
April 26.	0	0	0	8.5	8.5	8.5
April 28.	52.4	65.5	78.5	8.4	8.4	8.4
May 1.	186.1	177.1	128.5	8.5	8.6	8.6
May 3.	200.0	200.0	200.0	8.6	8.6	8.6
Second test						
May 6.	0	0	0	. . .	. . .	. . .
May 7.	20.3	20.3	20.3	8.8	8.8	8.8
May 9.	32.7	33.9	55.2	8.8	8.8	8.8
May 11.	157.1	151.8	151.8	8.6	8.6	8.6

*Total NaNO₂ present 200 mgm.

TABLE 2

The oxidation of $(NH_4)_2SO_4$

DATE	(NH₄)₂SO₄* OXIDIZED TO NITRITE IN TRIPLICATE SAMPLES			REACTION		
	1	2	3	1	2	3
	mgm.	mgm.	mgm.	pH	pH	pH
April 26.	0	0	0	7.1	7.1	7.1
April 28.	0	8.98	2.8	7.1	7.0	7.0
May 1.	2.6	21.3	Trace	7.1	6.6	6.6
May 3.	8.4	22.0	Trace	6.9	6.4	6.9
May 5.	17.2	24.3	Trace	6.8	6.4	6.8
May 6.	29.4	26.0	Trace	6.6	6.3	6.9
May 7.	31.8	26.0	2.3	6.5	6.4	6.9
May 9.	36.0	26.0	4.3	6.2	6.4	6.5
May 15.	44.1	. . . .	. . .	6.2	. . .	. . .

*Total (NH₄)₂SO₄ present 200 mgm.

For the first five days only a trace of nitrite was observed. Then the amount of nitrite increased more rapidly in two of the cultures, while culture no. 3 did not show much activity until the end.

The explanation was to be found in the reaction of the medium which was determined every time the solution was tested for nitrite. The solution was

about neutral at the start and as the activity of the organism increased the acidity of the solution increased. Since there was no base supplied the acid could not be neutralized.

The results indicated that even the neutral solution does not support much activity and whatever oxidation occurred was very slow.

In the following experiment with ammonia oxidation, the solution was supplied with an excess of $MgCO_3$ to react with the acid produced.

As will be seen from table 3 culture no. 1 oxidized all of the ammonium sulfate in 11 days. Its rate of oxidation was about 18 mgm. per day. In cultures 5 and 6 mono-and di-basic phosphates respectively were used. Evidently there was not much difference between the two forms of phosphorus.

TABLE 3

The oxidation of $(NH_4)_2SO_4$ in the presence of $MgCO_3$

CULTURE NUMBER	DATE	$(NH_4)_2SO_4$ OXIDIZED TO NITRITE	REACTION
		mgm.	*pH*
1	May 28	0	8.1
1	June 9	200.0	8.1
5 (KH_2PO_4)	June 7	0	8.1
5	June 15	105.0	7.3
6 (K_2HPO_4)	June 7	0	8.1
6	June 15	101.2	7.4

$MgCO_3$ as a base in the oxidation of $(NH_4)_2SO_4$ in solution cultures of nitrite formers was quite without any of the injurious effects as observed by Löhnis and Green (6) or Gaarder and Hagem (5) who tried both $MgCO_3$ and $CaCO_3$ as buffer for their media. The results reported there are in agreement with the recommendation and usage of Winogradsky (14).

Reaction of media

Table 2 clearly indicates that ammonia oxidation takes place very slowly or not at all at pH 7. From the results of table 3 it is plain that at pH 8 intense nitrification takes place. Gaarder and Hagem (5) have shown from their experiments that the optimum for nitrite production is at pH 7.9. Meyerhof (9) on the other hand obtained the maximum nitrite formation at pH 8.4.

Very rapid oxidation of NO_2 takes place according to the results in Table 1 at the reaction of pH 8.5 to 8.8. This result is confirmed by the work of Meyerhof (9) who finds the optimum reaction for the nitrate former between pH 8.3 and 9.3. Gaarder and Hagem (5) obtained maximum oxidation of nitrite at pH 6.8 to 7.3.

To find out if it is possible to further accelerate the rate of oxidation of NH_3 by the nitrifying organisms, the apparatus described below and shown in figure 1 was devised. It was prepared so that it should include the benefit derived from aeration together with the advantage accruing from constantly changing the surface of liquid exposed to the attack of the organisms.

A tube 2.25 inches in diameter and 5 feet 2 inches in length was almost filled with pieces of marble of the size of peas. One end was closed by rubber stopper *S* through which passed tube *A* bent at right angles and projecting about 2 inches into the tube, and a straight glass tube *B* which did not project inside the tube any farther than the rubber stopper. At the other end of the tube a wad of glass wool *W* covering a length of three inches was packed moderately tightly on the column of marble. This end was closed with a rubber stopper through which two glass tubes passed. There was a space of one inch left between the glass wool and the rubber stopper. Tube *E* projected ¾ of an inch into this space and directly below it on the glass wool was placed a watch glass *C*.

Another tube 6 feet long and 2.25 inches wide was fitted similarly except that the marble was replaced by clean washed limestone of the size of split peas.
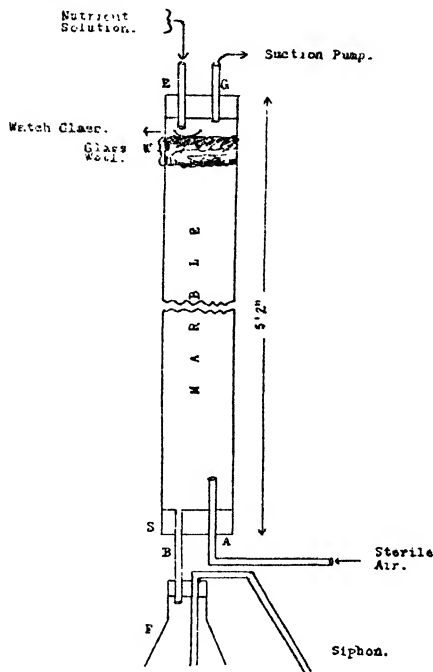
FIG. 1. DIAGRAM OF TUBE ARRANGED FOR OXIDATION OF AMMONIUM SULFATE

Both pieces of apparatus were wrapped in coarse linen and sterilized intermittently with steam. They were set up vertically with the glass wool ends at the top. The straight tube at the lower end was connected to a sterile flask *F* provided with a siphon arrangement. The bent tube was attached to a train of sterile water, sterile cotton and sterile sulfuric acid through which air was drawn. At the upper end tube *E* was connected by a siphon with supply of a sterile ammonium sulfate nutrient solution (no. 1). Tube *G* was connected to the suction pump. To establish a flora of nitrite formers on the marble and on the limestone, 190 cc. portions of two cultures of vigorously oxidizing organisms were allowed to drip slowly through *E*.

A fresh nutrient solution of ammonium sulfate was then allowed to drip slowly through E and the suction pump started to draw air through the tubes. The rate of dripping was regulated to four large drops every three minutes. Samples of the solution collected at the bottom in the Erlenmeyer flasks were

TABLE 4

The oxidation of $(NH_4)_2SO_4$ in tubes

DATE AND TIME SAMPLES TAKEN	INTERVAL (RATE OF FLOW WAS 4 DROPS IN 3 MINUTES)	REACTION OF SOLUTION COLLECTED AT BOTTOM	$(NH_4)_2SO_4$ FOUND AS NO_2 PER LITER
	hours	*pH*	*mgm.*
With marble in tube			
July 5............................	18	6.6	439.0
July 7............................	48	6.6	613.5
July 9 (11 a.m.).....................	48	6.6	746.0
July 9 (6 p.m.).....................	7	7.0	1012.0
With limestone in tube			
July 5............................	18	6.6	232.4
July 7............................	48	6.6	381.65
July 9 (11 a.m.).....................	48	6.6	506.0
July 9 (5 p.m.).....................	7	7.0	716.0

TABLE 5

Oxidation of $(NH_4)_2SO_4$ in tubes

DATE	PERIOD RUN		RATE OF FLOW PER MINUTE	REACTION IN RECEIVER	AMOUNT OF LIQUID IN RECEIVER	$(NH_4)_2SO_4$ OXIDIZED IN PERIOD RUN	$(NH_4)_2SO_4$ OXIDIZED PER 24 HOURS	EQUIVALENT TO $(NH_4)_2SO_4$ OXIDIZE. PER 100
	hours	*min.*	*drops*	*pH*	*cc.*	*mgm.*	*mgm.*	*mgm.*
With marble in tube								
July 23....................	5	30	5	6.8	123	19.6	104.6	15.92
July 31....................	4	0	7	7.3	175	33.78	202.0	19.31
July 31 and August 1........	11	0	4.5	7.4	270	75.71	165.4	29.09
August 1....................	8	0	3	7.3	136	2.04	48.1	3.58
With limestone in tube								
July 23....................	5	30	5	6.7	230	32.96	175.8	14.3
July 31....................	4	0	7	7.5	160	22.75	136.5	14.2
July 31 and August 1........	11	0	9.5	7.7	480	139.60	304.5	29.0
August 1....................	8	0	3	7.5	150	106.00	318.0	17.1

taken at different periods and analyzed for nitrite. Table 4 shows the rate of oxidation of ammonium sulfate per liter of solution dripped during different intervals. The maximum rate of oxidation at the given rate of flow was observed in the tube with marble on July 9 between 11 a.m. and 6 p.m. when

266 mgm. of ammonium sulfate per liter were oxidized. This oxidation was caused partly by the organisms in the tubes and partly also by the organisms washed into the flask where the liquid has been accumulating for four days.

To determine the exact amount of ammonium sulfate oxidized per day and to lessen the effect of oxidation in the receiving flash, the outflow liquid was collected and removed for definite intervals, measured, analyzed, and the nitrite content calculated. As seen from table 5 the maximum rate of oxidation in the tube containing marble was 202 mgm. per day. In the tube containing limestone the organism attained a maximum rate of oxidation of 318 mgm. per day. This was assuming that the rate of oxidation throughout the rest of the day remained as high as it was during the eight hours the liquids were collected. This assumption, however, is not warranted because the rate of oxidation is quite irregular. This has been noticed by Bonazzi (2). Winogradsky (14) found that after twenty days, nitrification in one of his cultures remained stationary instead of showing progressive increase as it had done previously.

The washing down of organisms by the dripping liquid might also have had some influence in decreasing the rate of oxidation noticed August 1 in the tube with the marble.

The high rate of oxidation obtained in these experiments is a result of optimum aeration, removal of products of oxidation by the downward flow of liquid and exposing a large surface of liquid to the bacterial activity. Where aeration was practiced as in the case of milk-bottle experiments reported at the beginning less than 20 mgm. of ammonium sulfate was oxidized per day. However, comparisons between these two experiments and especially between those of two different investigators—unless the experiments are conducted on identically similar conditions of apparatus, inoculum, aeration, etc.—are likely to mislead.

CONCLUSIONS

1. When a current of air was passed through a liquid culture of nitrate former in pint milk bottles, 31.4 mgm. of sodium nitrate was oxidized per day

2. Under the same conditions 18 mgm. of ammonium sulfate was oxidized by nitrite formers.

3. When a nutrient solution of ammonium sulfate was allowed to drip into the top of a long tube containing limestone of the size of split peas on the surface of which a flora of nitrite formers had been established and a current of air was drawn through the mass, the rate of oxidation of ammonium sulfate reached the maximum of 318 mgm. per day.

4. Vigorous oxidation of ammonium sulfate by the nitrite formers took place when the reaction of the liquid medium was around pH 8.0. For the nitrate formers the optimum reaction was between pH 8.5 and 8.8.

5. Magnesium carbonate used as a base in the oxidation of ammonium sulfate was without any injurious toxic effect.

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THE EFFECT OF SOIL SUSPENSIONS UPON THE SOLUBILITY OF THE SULFATE RADICAL IN THE SYSTEM $Ca(OH)_2$–$CaSO_4$–H_2O

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INTRODUCTORY

It has been shown (7) that heavy additions of burnt lime have an effect opposite to that of magnesia upon lysimeter leachings of native sulfates from soil, particularly during the first two years (4) after treatment. With increase in lime additions the losses of sulfates derived from soil, rainfall, and treatment-impurities were initially depressed far below the loss from untreated soil. From a related study (6) of sulfur precipitation, it was determined further that the sulfate concentrations of leachings from the heavily limed surface soil were decidedly less than those of the rain waters responsible for leachings. In a later report (8) it was shown that heavy CaO additions were also depressive to outgo of sulfates from three sulfureous treatments, $FeSO_4$, pyrite, and powdered sulfur, each equivalent to 1000 pounds of S per 2,000,000 pounds of soil. The $FeSO_4$ findings militated against the assumption that the depression exerted by CaO upon outgo of sulfates was the result of inhibited sulfofication of native or added sulfur.

But with increase in magnesia additions the sulfate losses were materially increased when no sulfur, save that of rainfall and impurities in treatments, was added to the soil. Magnesia, both light and heavy treatments, also accelerated the outgo of sulfates from additions of $FeSO_4$ and elementary sulfur (8). It was shown further (7) that light applications of both lime and magnesia accelerated the outgo of sulfates derived from native organic forms of sulfur and rainfall and also from ferrous sulfate and elementary sulfur. The reverse was true, however, where pyrite was added. The loss from pyrite alone exceeded that from pyrite supplemented by both light and heavy amounts of CaO and MgO.

In one of the contributions (6) above cited, the data of Cameron and Bell (2) and Seidell (9) were given in parallel with similar data obtained by two analysts in this laboratory to demonstrate that the solubility of $CaSO_4$ was less in the system $Ca(OH)_2$–$CaSO_4$–H_2O than in the system $CaSO_4$–H_2O. Though the influence of $Ca(OH)_2$ upon the solubility of $CaSO_4$ without contact with soil was positive, it was still insufficient by far to account for the greatly diminished outgo of added sulfates in the lysimeter leachings. The work here reported

was done in an effort to determine the cause for the failure of both added and engendered sulfates to leach from surface soil alone, even after 5 years.

EXPERIMENTAL

As a preliminary step, two points were determined empirically:

A. Absolute occurrences of SO_4 in varying charges of commercial high-calcic lime.

TABLE 1

*Influence of variation in charge upon the hydrochloric acid soluble sulfates in a high-calcic commercial hydrated lime**

CHARGE OF COMMERCIAL SAMPLE	CaO DISSOLVED AS CaCl$_2$	SULFATE FOUND AS BaSO$_4$ EQUIVALENT	
		Per charge	Per 100 gm. of sample.
gm.	*gm*	*gm.*	*gm.*
1.66	1.137	0.0290	1.75
3.33	2.281	0.0561	1.69
5.00	3.425	0.0860	1.72
6.67	4.568	0.1132	1.70
13.34	9.137	0.2270	1.70
21.20	14.522	0.3590	1.70

* BaSO$_4$ precipitated from a uniform volume of 400 cc.

TABLE 2

*Influence of variation in charge upon the water extractable sulfate in a high-calcic commercial hydrated lime**

CHARGE OF COMMERCIAL SAMPLE PER LITER OF H$_2$O	Ca(OH)$_2$ PER LITER		WATER SOLUBLE SULFATES AS BaSO$_4$	
	In solution phase	Undissolved excess of solid phase	Per liter of extract	Per 100 gm. of sample
gm.	*gm.*	*gm.*	*gm.*	*gm.*
1.66	1.296	0.118	0.0248	1.499
3.33	1.740	1.106	0.0320	0.961
5.00	1.740	2.520	0.0482	0.964
6.67	1.776	3.894	0.0574	0.860
13.34	1.776	9.590	0.0980	0.720
21.20	1.776	16.286	0.1580	0.745

* BaSO$_4$ precipitated from a uniform volume of 400 cc.

B. Amount of water-soluble $CaSO_4$ recoverable from each of the several charges of the commercial hydrate used alone and with soil in subsequent experiments.

Total SO_4 was determined by making hydrochloric acid solutions of charges ranging between 1.66 gm. and 21.20 gm., barium sulfate precipitations being made from a constant volume of 400 cc. No evidence of H_2S was detected during the boiling of lime with hydrochloric acid.

A. Total SO_4 in $Ca(OH)_2$. The actual charges, CaO as $CaCl_2$ in the HCl solution, $BaSO_4$ determined and $BaSO_4$ per 100 gm. of sample are given in table 1. These results show a constant well within analytical error, and they give no indication of calcium occlusion by the $BaSO_4$ precipitate.

B. Water-soluble SO_4 in $Ca(OH)_2$. Charges 1.5 times those designated in table 1 were then used for 1.5-liter aqueous extractions of sulfate impurities. Titrations were made against 25-cc. aliquots to determine the respective concentrations of $Ca(OH)_2$. Aliquots of 500 cc. were used for duplicate $BaSO_4$ precipitations, the 500-cc. aliquots having been first acidified slightly with HCl and reduced to a constant volume of 400 cc. The $BaSO_4$ occurrence per liter is on the same basis as the total $BaSO_4$ found per corresponding proportionate charges in table 1. The resulting data are given in table 2.

The results of table 2 show a uniform $Ca(OH)_2$ concentration for all charges above the minimum of 1.66 gm. The solid-phase excesses of $Ca(OH)_2$ are given, along with $BaSO_4$ determinations and the calculations on the basis of 100 gm. of charge. The maximum recovery per 100 gm. of lime is less than the maximum in the hydrochloric acid solution. The maximum recovery in each case was obtained from the solution of minimum charge. However, varying from the hydrochloric acid solutions, where the doubling of the charge gave a sulfate recovery slightly less than twofold and probably within analytical error, the doubling of the minimum charge in the aqueous solution caused a very decided drop in the ratio of sulfate recovered to charge used. Further decreases in respective proportions of SO_4 recovered are also shown for increases in bulk of undissolved hydrate. These data demonstrate one point which should interest the commercial chemist and analyst as well as the soil chemist. Water-soluble sulfates can not be determined as a constant in burnt and hydrated high-calcic limes, at least within the time limits designated, since the mass of the solid-phase $Ca(OH)_2$ is a factor as well as saturation of the lime water solution. The measure of sulfates must be the concentration of the unoxidized HCl solution (or equivalent solvent), the calcium concentration of which seems to be of no import within the ranges of 1.66 gm. to 21.20 gm. per liter.

SOLUBILITY OF $CaSO_4$ DERIVED FROM $FeSO_4$ IN $Ca(OH)_2$ SOLUTIONS WITH AND WITHOUT SOIL

We do not know of previous work upon the influence of lime as affecting extractability of soil sulfates. In their studies upon the determination of sulfates in alkali soils, however, Hirst and Greaves (3) state: "In our work on the nitrates . . . . and chlorides . . . . clarifying agents, such as alum and lime, were used with excellent results. For obvious reasons, however, neither of these substances could be used for clarifying solutions in which sulfates are to be determined, particularly if there were any appreciable amounts of sulfate present as is the case with many alkali soils."

In studying the influence of solution and solid-phase excesses of $Ca(OH)_2$ upon the sulfate radical, with and without soil, $FeSO_4$ solutions were used in experiments 1–4, 6, and 7. In agreement with the sulfate additions in the previous lysimeter studies (8) ferrous sulfate additions were made at the rate of 1000 pounds of S per 2,000,000 pounds of soil. The following experiments were carried out, all solutions having been placed in closed containers, unless otherwise stated.

Experiment 1. Immediate addition of lime to aqueous $FeSO_4$-soil suspensions

Each of three charges of $FeSO_4$, equivalent to 0.2500 gm. of sulfur, was dissolved in 3.5 liters of water. To each of these solutions 500 gm. of soil were added and the mixture was thoroughly agitated. Four grams of the commercial hydrate was then added to one solution, 16 gm. to the second, and 50 gm. to the third. The three admixtures were then shaken thoroughly every thirty minutes for seven hours and permitted to stand undisturbed overnight. These three immediate additions of CaO were representative of the 8-, 32-, and 100-ton additions reported upon (7) previously.

A. Aliquots of each supernatant solution were then titrated against phenolphthalein to determine the respective concentrations of $Ca(OH)_2$. Sulfates were also determined upon 500-cc. aliquots, the clear solutions having been first acidified slightly with HCl and concentrated to a volume of 400 cc.

B. The remaining portion of each admixture was again agitated every thirty minutes for a period of seven hours and permitted to stand overnight undisturbed, with repetition of the $Ca(OH)_2$ and sulfate determinations.

C. The residues from B were then permitted to stand for 14 days, being agitated once each day, after which the analytical procedure of A and B was carried out. The sulfate recoveries thus obtained are given in table 3.

The recoveries of A, B, and C are given as grams of $BaSO_4$ per 500 cc. aliquots and as percentages of the respective sulfate totals. Those totals represented the addition-constant plus the determined water-soluble SO_4 variables from the impurities contained in the $Ca(OH)_2$. The 98 per cent recovery of SO_4 from the 8-ton treatment increased to over 100 per cent for both the 48-hour and 16-day intervals. Though the concentration of $Ca(OH)_2$ from the unabsorbed excess of $Ca(OH)_2$ in the 8-ton treatment was only a small fractional part of that from the 32- and 100-ton treatments, and though it decreased decidedly with lengthened period of contact, the causticity and lack of aeration were such as to inhibit biochemical oxidation of the organic sulfur of the soil, and it would therefore seem that the greater recoveries over the longer periods were due to further releases of accumulated soil sulfates. The two heavier additions proved progressively repressive upon sulfate solubility both as to increase in $Ca(OH)_2$ additions and period of contact of soil with $Ca(OH)_2$. With less frequent agitation during the last fourteen days, the three soil suspensions caused definite decreases in the concentrations of the supernatant $Ca(OH)_2$ solutions. The very small recoveries from the two heavier

admixtures of lime with soil were very much less than the water-soluble blanks of table 2, showing that the soil-lime suspensions removed from the solution phase not only the added soluble sulfate, but also most of that carried as impurities in the calcium hydrate—an effect which increased with increase in time of contact.

TABLE 3

Sulfate recovery from aqueous solutions of $FeSO_4$ in soil suspensions, as influenced by immediate additions of $Ca(OH)_2$ (experiment 1)

$Ca(OH)_2$ ADDITION AS CaO-EQUIVALENT PER 2,000,000 LBS. OF SOIL	TITRATION 0.5 N ACID PER 500 CC. AGAINST PHENOL-PHTHALEIN AFTER			BaSO₄ EQUIVALENT IN 500 CC.			BaSO₄ PRECIPITATE FROM 500 CC. ALIQUOTS AFTER ADDITION OF LIME*					
							After 24 hours A		After 48 hours B		After 16 days C	
	24 hours	48 hours	16 days	Added as FeSO₄ in solution	As impurities in charge	Total actually present	Per 500 cc. aliquot	Of total present	Per 500 cc. aliquot	Of total present	Per 500 cc. aliquot	Of total present
tons	cc.	cc.	cc.	gm.	gm.	gm.	gm.	per cent	gm.	per cent	gm.	per cent
8	6.5	3.0	0.9	0.2650	0.0135	0.2785	0.2730	98.0	0.3006	107.9	0.3135	112.2
32	39.5	35.0	28.0	0.2650	0.0540	0.3190	0.0475	14.8	0.0220	6.9	0.0092	2.9
100	44.5	43.5	38.0	0.2650	0.1688	0.4338	0.0470	10.8	0.0137	3.2	0.0070	1.6

* Average of six determinations FeSO₄-soil control immediately before addition of lime 0.2207 and 24 hours later without lime 0.2145.

TABLE 4

Sulfate recovery from aqueous solutions of $FeSO_4$ in soil suspensions to which lime was added 24 hours after a 24-hour preliminary contact of $FeSO_4$ solution with soil (experiment 2)

$Ca(OH)_2$ ADDITION AS CaO-EQUIVALENT PER 2,000,000 LBS. OF SOIL	TITRATION 0.5 N ACID PER 500 CC. AGAINST PHENOLPHTHALEIN AFTER		BaSO₄ EQUIVALENT IN 500 CC.			BaSO₄ PRECIPITATE FROM 500 CC. ALIQUOTS AFTER ADDITION OF LIME*			
						After 24 hours		After 15 days	
	24 hours	15 days	Added as FeSO₄ in solution	As impurities in charge	Total actually present	Per 500 cc. aliquot	Of total present	Per 500 cc. aliquot	Of total present
tons	cc.	cc.	gm.	gm.	gm.	gm.	per cent	gm.	per cent
8	1.8	1.0	0.2650	0.0135	0.2785	0.2760	99.1	0.3085	110.8
32	38.0	29.0	0.2650	0.0540	0.3190	0.0230	7.2	0.0070	2.2
100	44.5	38.0	0.2650	0.1688	0.4338	0.0155	3.6	0.0052	1.2

* Average of six determinations no-soil control 0.2207 gm. after 24 hours and 0.2145 gm. after 48 hours.

Experiment 2.   Twenty-four-hour contact of $FeSO_4$ with soil suspensions before addition of $Ca(OH)_2$

In this experiment the charges and sulfate concentrations were the same as those of experiment 1.   In each case the FeSO₄ solution was agitated every

half hour with 500 gm. of soil and permitted to stand overnight, after which the lime additions were made and the procedure of experiment 1 was carried out as to titrations and $BaSO_4$ determinations.

The sulfate solutions which were brought into contact with the soil suspensions in the present experiments were well below the saturation of $CaSO_4$. This obtained where the $CaSO_4$ was formed from reaction between $Ca(OH)_2$ and $FeSO_4$, and also where added later as the solid-phase $CaSO_4 \cdot 2H_2O$.

It would be expected that full proportional recovery would have obtained in the 500-cc. aliquots from the soil-$FeSO_4$ controls. The effect of the $FeSO_4$, if not that of $CaSO_4$, also, would be to flocculate the soil suspensions as would an addition of a dilute acid solution upon an acid soil. Brown and Kellog (1) found that a similar condition—sulfate extraction with a dilute HCl solution—resulted in a sulfate recovery below that obtained by water. This was true of both native sulfates and added $MgSO_4$. The failure of the added soluble sulfate of iron to leach from the lysimeters (8), when added alone and with supplements of CaO and MgO after having been subjected to a total rainfall of 256.0 inches over a 5-year period, indicates that the soil-to-water proportions and the agitated suspension conditions imposed by Brown and Kellog, and by us in the present experiments, were more effective than rainfall leachings in removing sulfates from the soil mass. This point will be considered more at length in concluding paragraphs.

The data of table 4 show decreases in $Ca(OH)_2$ concentrations of the supernatant solution similar to those shown in table 3. It also appears that the longer period of contact of $FeSO_4$ solution with soil and delayed addition of CaO gave results corresponding to those obtained with immediate additions of both $FeSO_4$ solution and lime charges to the soil suspensions. This was true for all three rates of lime treatment.

The results of experiments 1 and 2 (tables 3 and 4) show that the soil mass held the added soluble sulfate against the extractions as tenaciously as it did against rainfall leachings in the lysimeters. Those leachings studies (7) showed a parallel between the formation of $CaCO_3$ from added CaO and the release of the sulfate additions to the drainage waters. This transition in the field lysimeters was, however, a matter of months. Experiment 3 was therefore carried out to determine any change in the retentive properties of the soil, as influenced by the immediate reversion of CaO to $CaCO_3$.

Experiment 3.   Effect of early conversion of $Ca(OH)_2$ to $CaCO_3$ upon retention of SO_4 by soil suspensions

In this experiment the same charges and concentrations obtained as in experiments 1 and 2. The soil suspensions were twice agitated with the $FeSO_4$ solution during one hour's preliminary contact. The CaO additions were then introduced, the admixtures agitated every half hour for 7 hours, and permitted to stand overnight. Aliquots of 500 cc. in duplicate, were withdrawn and the $Ca(OH)_2$ concentrations and sulfate contents determined.

Solid Na_2CO_3 was then added in slight excess of the amount required to convert all residual $Ca(OH)_2$ to $CaCO_3$. The frequent agitations, overnight standing, and $BaSO_4$ determinations of experiments 1 and 2 were then carried out. The NaOH formed by the reaction of $Ca(OH)_2$ with Na_2CO_3 gave a highly colored supernatant liquid. This contained large quantities of silica, iron, and organic matter, which were filtered with difficulty. One point should be stressed. In soil-lime suspensions the soil colloids were not in evidence; but the hydrated lime represented a mass of material in colloidal and near-colloidal state. On the other hand, after addition of Na_2CO_3 all of the lime was removed from solution as the carbonate, while a large mass of soil materials were dispersed in the colloidal state throughout the liquid medium.

The $BaSO_4$ determinations and percentage recoveries of total sulfates supplied by additions and as treatment-impurities are given in table 5.

TABLE 5

Sulfate recovery from aqueous solutions of $FeSO_4$ plus early additions of excesses of solid phase $Ca(OH)_2$* in soil suspensions before and after conversion of $Ca(OH)_2$ additions into $CaCO_3$ (experiment 3)

Ca(OH)₂ ADDITION AS CaO-EQUIVALENT PER 2,000,000 LBS. OF SOIL	BaSO₄ EQUIVALENT IN 500 CC. ALIQUOTS AS SUMS OF A CONSTANT EQUIVALENT ADDITION OF 0.2650 GM. PLUS VARIABLE CHARGE IMPURITY	BaSO₄ PRECIPITATE FROM 500 CC. ALIQUOTS					
		24 hours after addition of Ca(OH)₂ to FeSO₄ solution in contact with soil		Following addition of slight excess of Na₂CO₃ to FeSO₄-Ca(OH)₂ soil suspensions			
				After 24 hours		After 15 days	
		Per 500 cc, aliquot	Of that present	Per 500 cc. aliquot	Of that present	Per 500 cc. aliquot	Of that present
tons	*gm.*	*gm.*	*per cent*	*gm.*	*per cent*	*gm.*	*per cent*
8	0.2785	0.2670	95.9	0.3194	114.7	0.3390	121.7
32	0.3190	0.1000	31.3	0.3336	104.6	0.3585	112.4
100	0.4338	0.1010	23.3	0.3670	84.6	0.4393	101.5

* $Ca(OH)_2$ added after 1 hour's contact between $FeSO_4$ solution and soil suspensions.

These data show that the depressive influences of the excess of $Ca(OH)_2$ were in effect upon the added sulfate radical at the end of the preliminary period of 24 hours. As in similar cases in tables 3 and 4, it could not be concluded that the SO_4 decreases are due to the formation of double salts of calcium and iron, for the same result will be shown where the sulfate radical was introduced as $CaSO_4$. But, after a further 24-hour period of contact following the addition of sodium carbonate, the recoveries from the 8-ton and 32-ton treatments were in excess of the respective amounts known to have been introduced as $FeSO_4$ and as treatment impurities. In the case of the 100-ton additions, the recovery was more than three times that obtained after the 24-hour contact of soil and heaviest excess of $Ca(OH)_2$. The agitations during the first twenty-four hours after introduction of Na_2CO_3 were apparently insufficient to bring all of the large excess of $Ca(OH)_2$ into reaction with the Na_2CO_3. Fourteen days later all of the calcium hydrate had apparently been

converted to $CaCO_3$, for the SO_4 recovery then obtained was equal to that supplied both as ferrous sulfate and as lime impurities. Ammonium carbonate produced the same nullifying effect as that produced by the added Na_2CO_3. The resultant solutions were filtered with such difficulty, however, that its use was abandoned.

The recoveries of sulfate after introduction of Na_2CO_3, or $(NH_4)_2CO_3$, might be attributed entirely, or in large part, to the solvent action of the NaOH, or $(NH_4)OH$, engendered through reaction between $Ca(OH)_2$, and Na_2CO_3 or $(NH_4)_2CO_3$, respectively, rather than to conversion of $Ca(OH)_2$ into $CaCO_3$, were it not for the fact that the same result was obtained by aqueous extraction when the excess of $Ca(OH)_2$ was converted to $CaCO_3$ by means of passages of CO_2 into the $Ca(OH)_2$-soil suspensions. After preliminary contact, one of the 32-ton $Ca(OH)_2$-soil admixtures was subjected to a continuous flow of CO_2 with frequent agitations until all hydrate had become carbonated. From the total sulfate addition of 0.3190 gm. $BaSO_4$ equivalent per 500 cc. of 0.2650 gm. derived from the $FeSO_4$ and 0.0540 gm. as impurities in the $Ca(OH)_2$, the recoveries obtained were as follows:

	gm.
After 24 hours contact with $Ca(OH)_2$ and *just before* passage of CO_2	0.1000
Immediately after conversion of $Ca(OH)_2$ into $CaCO_3$ by passage of CO_2	0.3638
Increased recovery due to the carbonate reaction	0.2687

The increase of 0.2687 gm. caused by the passage of CO_2 represents full recovery of the addition and demonstrates that most of the absorptive property of this soil for calcium sulfate passes immediately upon the disappearance of $Ca(OH)_2$. It is thus apparent that while in a hydrated condition from an excess of OH-ions supplied by $Ca(OH)_2$, the soil mass possessed marked retentive properties. It is equally apparent that it did not possess those retentive properties when the OH-ions were supplied by NaOH generated by the $Ca(OH)_2$ and Na_2CO_3 reaction.

The sulfate retention in the soil-$Ca(OH)_2$ suspensions could not well be assigned to $Fe_2O_3 \cdot nH_2O$ derived from the ferrous sulfate, because of the small amount so derived, especially since the containers were sealed. This point will be considered further in experiment 7 (table 9).

Experiment 4.   Effect of delayed conversion of $Ca(OH)_2$ to $CaCO_3$ upon retention of SO_4 by soil suspensions

This experiment corresponded to experiment 2, where the $FeSO_4$ was in contact with the soil prior to the introduction of $Ca(OH)_2$, which was converted, 24 hours later, to $CaCO_3$ by means of additions of solid-phase Na_2CO_3. Data obtained are given in table 6. These results show an incomplete recovery of the total sulfate additions after the soil alone had been in contact with the $FeSO_4$ solution for the preliminary period of 24 hours prior to the addition of $Ca(OH)_2$. This partial retention of the SO_4 added to the acid soil is in harmony with the previous lysimeter findings (7) relative to the incomplete leaching of

the acid salt from the same acid soil after extended periodic leaching by rain water.   The gains in $BaSO_4$ recoveries which followed conversion of the excesses of $Ca(OH)_2$ into $CaCO_3$ show the same order which obtained in experiment 3, where the $Ca(OH)_2$ additions were made almost immediately after the soil charges were suspended in the $FeSO_4$ solutions.

Experiment 5.   Influence of $Ca(OH)_2$ solutions upon solubility of freshly precipitated $CaSO_4 \cdot 2H_2O$ with and without soil

In the previous experiments, here reported, the sulfate radical was introduced as $FeSO_4$, in conformity with the sulfate additions to the lysimeters.   The reaction between $FeSO_4$ and the excesses of $Ca(OH)_2$ produced $CaSO_4$ in the present experiments and also in the leachings from the lysimeters.   In experiment 5, freshly precipitated $CaSO_4 \cdot 2H_2O$ was used as the source of SO_4 in tests

TABLE 6

Sulfate recovery from aqueous solutions of $FeSO_4$ in soil suspensions,* the subsequent recoveries after adding excess of $Ca(OH)_2$† and the converting all $Ca(OH)_2$ to $CaCO_3$ (experiment 4)

AS $Ca(OH)_2$ ADDITION CaO-EQUIVALENT PER 2,000,000 LBS. OF SOIL	BaSO$_4$ EQUIVALENT PRESENT IN 500 cc. ALIQUOT, AS SUMS OF A CONSTANT FeSO$_4$ SOLUTION AND IMPURITY VARIABLES	BaSO$_4$ PRECIPITATE FROM 500 CC. ALIQUOTS					
		From soil suspensions after 24-hour contact of soil and FeSO$_4$ without lime		From soil plus Ca(OH)$_2$ plus Na$_2$CO$_3$			
				24 hours after preliminary period of contact of FeSO$_4$ with soil		15 days after preliminary period of contact of FeSO$_4$ with soil suspensions	
		Found	Loss	Found	Gain‡	Found	Gain‡
tons	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*
8	0.2785	0.2350	0.0435	0.3430	0.1080	0.3515	0.1165
32	0.3190	0.2115	0.1075	0.3450	0.1335	......	......
100	0.4338	0.2210	0.2128	0.3410	0.1200	0.4090	0.1808

* $FeSO_4$ in contact with soil suspensions 24 hours before addition of $Ca(OH)_2$.

† $Ca(OH)_2$ present with soil-$FeSO_4$ suspensions one hour before addition of Na_2CO_3.

‡ Over recoveries from $FeSO_4$ additions to soil suspensions.

to show the effect of excesses of $Ca(OH)_2$ upon the solubility of SO_4 in lime-water solutions and in aqueous soil-lime suspensions.   The calcium sulfate was made by addition of H_2SO_4 to aqueous solutions of chemically pure $CaCl_2$. A constant charge of 500 gm. of soil was used as before.   The $CaSO_4$ additions were made as aliquots equivalent to 0.0735 gm. $BaSO_4$ per 500-cc. aliquot.   The excesses of $Ca(OH)_2$ were added in quantities which represented equivalences of 8, 16, 24, 32, and 100 tons of CaO per 2,000,000 pounds of soil.   The results of table 7 give the respective totals of sulfate added, the sums of the addition constant and the impurity variables.   The recoveries from solutions and $Ca(OH)_2$ excesses alone and with soil are given, together with gram and per cent deviations from theoretical.   With increase in charge of $Ca(OH)_2$ in the system $Ca(OH)_2-CaSO_4-H_2O$ there was found a progressive increase in recovered sulfates, but a progressive increase also in the amounts undissolved.   These

unrecovered amounts ranged between 0.0123 gm., or 14.4 per cent, for the 8-ton addition and 0.0783 gm. or 34.8 per cent, for the 100-ton addition. Since all of the lime-water solutions were of equivalent concentration in the absence of soil, it is apparent that the bulk of solid-phase $Ca(OH)_2$ is of more import than the concentrations of the solution phase.

In the soil suspensions, the decreases in sulfate recoveries were still more extensive. Even with the water-soluble sulfates of the soil to draw from the recovery of the $CaSO_4$ from the no-lime control was only 81 per cent of that added. The minimum addition gave a recovery practically identical to the amount of $CaSO_4 \cdot 2H_2O$ added, though but 84.2 per cent of that added as sulfate plus $Ca(OH)_2$ impurities. Increase to the 16-ton rate caused a decrease in recovery, i.e., only 19.5 per cent of the total addition. The 24-, 32-, and 100-ton additions gave the still lower percentage recoveries of 6.2, 4.2, and 2.7 for respective possibilities.

TABLE 7

Influence of $Ca(OH)_2$ additions upon the recovery of SO_4 from an aqueous solution of $CaSO_4$* *and from the same solution in contact with a constant soil suspension (experiment 5)*

CaO EQUIVALENT PER 2,000,000 LBS. OF SOIL	BaSO₄ EQUIVALENT OF CALCIUM SULFATE PLUS Ca(OH)₂ IMPURITIES	BaSO₄ FROM 500 CC. ALIQUOT		DEVIATION FROM THEORETICAL			
		Lime plus CaSO₄ solution only	Lime, CaSO₄ solution and soil	Lime plus CaSO₄ solution only	Lime, CaSO₄ solution and soil	Lime and CaSO₄ solution only	Lime, CaSO₄ solution and soil
tons	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*	*per cen i*	*per cent*
None	0.0735	0.0735	0.0595	. . . .	−0.0140	. . . .	−19 0
8	0.0855	0.0732	0.0720	−0.0123	−0.0135	−14.4	−15.8
16	0.0975	0.0785	0.0190	−0.0190	−0.0785	−18.5	−80 5
24	0.1095	0.0895	0.0068	−0.0200	−0.1027	−18.3	−93.8
32	0.1215	0.0916	0.0051	−0.0299	−0.1164	−24 6	−95 8
100	0.2255	0.1470	0.0161	−0.0785	−0.2194	−34.8	−97.3

* Freshly precipitated from aqueous $CaCl_2$ solution—constant of 0.0735 gm. BaSO⁴ equivalent.

Experiment 6. Influences of calcium and magnesium hydrates and carbonates upon SO_4 solubility, with and without soil

In earlier lysimeter investigations (5,7) it was found that increased additions of both MgO and $MgCO_3$ caused increases in the outgo of sulfates derived from soil and rainfall. The same finding was later obtained (8) when soluble sulfate and elementary sulfur additions were made. Differing from equivalent treatments of CaO, increases in both $CaCO_3$ and limestone were followed by no depressive effects upon sulfate leachings. In view of those findings the oxides of calcium and magnesium were compared with the corresponding carbonates as to their influence upon the retention of sulfates by the soil of experiments 1-5, which was also used in the above cited lysimeter investigations. The four materials were used in amounts chemically equivalent and at the three rates

used in the lysimeter investigations.   Uniform charges of 500 gm. of soil and a dissolved $FeSO_4$ constant of 0.2695 gm. $BaSO_4$-equivalence per 500 cc. were used in 4-liter suspensions of soil and alkali-earths.   The recoveries from the four series with and without soil are given in table 8—each result being the average of duplicate determinations upon 500-cc. aliquots.

The recoveries from the $FeSO_4$ additions to the three $Ca(OH)_2$ charges without soil are fairly close.   All were less than the amount added in the form of $FeSO_4$, the compensating factors of decreased solubility and increased sulfate impurities being in effect.   But, when soil was added there followed a very extensive decrease in sulfate recovery from both 32-ton and 100-ton additions. The difference between the 8-ton and 100-ton recoveries amounted to 0.2605 gm. $BaSO_4$ equivalent.

TABLE 8

Comparison of $Ca(OH)_2$, $CaCO_3$, $Mg(OH)_2$ and $MgCO_3$ additions upon the solubility of SO_4 radical in $FeSO_4$ solution with soil suspensions, (experiment 6)*

CaO EQUIVALENT PER 2,000,000 POUNDS OF SOIL	BaSO₄ PRECIPITATE FROM 500 CC. ALIQUOTS OF FeSO₄ SOLUTION AND ADDITIONS OF ALKALI-EARTHS WITH AND WITHOUT SOIL							
	$Ca(OH)_2$		$CaCO_3$		$Mg(OH)_2$		$MgCO_3$	
	After 24 hours contact without soil	After 24 hours contact with soil	After 24 hours contact without soil	After 24 hours contact with soil	After 24 hours contact without soil	After 24 hours contact with soil	After 24 hours contact without soil	After 24 hours contact with soil
tons	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*
8	0.2360	0.2760	0.2773	0.3092	0.2550	0.3135	0.2664	0.3218
32	0.2385	0.0230	0.2755	0.3155	0.2355	0.3005	0.2735	0.3370
100	0.2400	0.0155	0.2695	0.3594	0.2020	0.3100	0.2910	0.3664

*$BaSO_4$ equivalent of 500 cc. of aqueous $FeSO_4$ solution, 0.2695 gm.

On the other hand, the three corresponding $CaCO_3$ additions not only gave concordant recoveries equivalent to, or greater than, the sulfate added in solution in the absence of soil, but they also gave increases above the additions in all cases where the soil mass was present.   Thus, the increasing charges of $CaCO_3$ either caused the formation of additional soluble sulfates or decreased the soil's tendency to retain sulfates.

In the case of the MgO addition to $FeSO_4$ solutions without soil, the bulk of undissolved light oxide exhibited a more repressive action than that shown by the excess of $Ca(OH)_2$.   In no case was the recovery equivalent to the addition of soluble sulfate.   The repression was even more marked because of the smaller amount of sulfate impurities in the MgO and the more marked decrease from the 0.2695 gm. constant, the decrease being, therefore, more in progression, as well as in corresponding totals.   The decreased recovery resulting from increase in charge of MgO was chargeable to the sulfate addition, rather than the sulfate impurities of the magnesium oxide.   This was determined by the proportionate recoveries of 0.0015 gm., 0.0030 gm. and 0.0068 gm. $BaSO_4$ from MgO charges of 5, 10, and 20 gm., respectively.

However, the introduction of soil was followed by an increase above the 0.2695 gm. constant, rather than the decrease shown by the $Ca(OH)_2$-soil admixtures. It is evident, therefore, that the increase in hydroxyl-ion concentration caused by the $Mg(OH)_2$ produced a different effect from that caused by the hydroxyl-ion increase induced by $Ca(OH)_2$ in the soil suspensions. The concentration of $Mg(OH)_2$, however, was far less than that of $Ca(OH)_2$.

The use of equivalent amounts of hydrated $MgCO_3$ at the three rates, without soil, gave recoveries approximating, or exceeding, the constant addition of 0.2695 gm. $BaSO_4$ equivalent. Where the 500-gm. constant of soil was introduced the recoveries were in all cases in excess of the sulfate addition, and considerably in excess of corresponding recoveries from the respective equivalents of MgO. In harmony with the sulfate recoveries afforded by the several treatments in the lysimeters (7, 8), the $MgCO_3$ proved to be most active in causing the soil to release sulfates to aqueous extractions.

Experiment 7. Influence of aeration and incidental agitation upon tendency of excesses of $Ca(OH)_2$ to inhibit recovery of SO_4

In the discussion of data of experiment 3, mention was made of the possible occlusive action which might be attributed to the small amount of hydrated ferric oxide derived from the ferrous sulfate, in case of its oxidation. This point was considered further. Three charges of $Ca(OH)_2$ were added to 400-cc. portions of $FeSO_4$ in 500-cc. flasks and the flasks connected en train. The CaO equivalences of the three charges are given in table 9. In order to permit observation of color changes, no soil was added to the three charges of $Ca(OH)_2$. Air was drawn through an aqueous guard solution and into the three flasks with such rapidity as to insure constant suspension of the charges during a 24-hour period. The 100-cc. aliquots were then withdrawn and sulfates determined, in parallel with 500-cc. aliquots from a comparable series of larger volume. The larger containers of the parallel series were shaken each half hour for 7 hours and permitted to stand overnight. The results are given in table 9.

Upon settling, all three clear supernatant liquids from the aspirated mixtures were free of iron. A yellowish color soon appeared in the hydrate precipitate of minimum treatment in the first flask in the series. No such color was observed in the two larger additions. It seemed probable, therefore, that the ferrous oxide from the $FeSO_4$ had been converted into the hydrated ferric oxide in all three flasks and that the larger bulk of white hydrate was sufficient to mask the amount of hydrated ferric oxide derived from the ferrous sulfate addition. Additions of freshly precipitate hydrated ferric oxide were therefore introduced into the largest lime suspension in the 500-cc. flask, which was then sealed. A yellowish color prevailed at first, as in the case of the minimum charge after aspiration. This fawn color faded gradually, however, and after one week had entirely disappeared. The point arises whether this change is to be attributed to chemical or physical causes, or to a combination of the two.

Because of the small occurrence of silica, and that most probably as calcium silicate, the small occurrence of insoluble magnesium oxide, and the large active mass of $Ca(OH)_2$, any possible insoluble double salt responsible for SO_4 precipitation would probably be one formed by calcium-iron or calcium-aluminum combination.   It will be shown that insoluble ignited Fe_2O_3 undergoes considerable hydration when suspended in solutions of $Ca(OH)_2$.   It therefore seems hardly probable that the removal of both Fe and SO_4 from solution was caused by the formation of an insoluble colorless precipitate, calcium-iron sulfate.   It seems more plausible to assume that the reddish hydrated oxide particles are masked while serving as nuclei for a progressive deposition of $Ca(OH)_2$ of fineness equivalent to, or approaching, the colloidal state.   It may be assumed that both experimental conditions, minimum of contact with maximum agitation and maximum of contact with minimum agitation tend to produce greater dispersion—finer and finer subdivision, i.e. increase in both colloidal state and

TABLE 9

Sulfate recovery from aqueous solutions of $FeSO_4$, as influenced by additions $Ca(OH)_2$ with and without aeration (experiment 7)

CaO ADDITIONS, AS HIGH CALCIC COMMERCIAL LIME PER 500 cc.	BaSO$_4$ EQUIVALENT IN 500 CC.			BaSO$_4$ PRECIPITATE FROM 500 CC. ALIQUOTS AFTER 24 HOURS CONTACT OF FeSO$_4$ SOLUTION WITH LIME			
	Added as FeSO$_4$ in solution	As impurities in lime charge	Total	Periodic agitation and no aeration		Constant agitation and aeration by means of aspiration	
				Found	Unrecovered	Found	Unrecovered
gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.
0.8000	0.2650	0.0135	0.2785	0.2360	0.0425	0.2090	0.0695
2.2857	0.2650	0.0540	0.3190	0.2385	0.0805	0.1660	0.1530
7.1428	0.2650	0.1688	0.4338	0.2400	0.1938	0.1940	0.2398

extreme subdivision approaching that state.   With its great surface exposure, hydrated iron oxide would attract sufficient of such finely divided material, thereby becoming covered to the point of loss of its inherent color.   Again, under the dynamic conditions of saturated solution over large excesses of solid-phase $Ca(OH)_2$ the continuous passage of the solid phase hydrate into solution phase and the reciprocal precipitation of $Ca(OH)_2$ from solution phase into solid phase may cause cumulative deposition of the white hydrate over the yellow surface of the hydrated ferric oxide, causing the yellow to be masked—time and agitation both tending to hasten the masking effect.

The analyses of table 9 show incomplete recovery of the sulfate present in each $Ca(OH)_2$ suspension, for both periodic agitation without aeration and constant agitation and aeration through aspiration.   With increase in mass of solid phase $Ca(OH)_2$ the amounts of unrecovered SO_4 also increased.   The unrecovered fractions of sulfates were consistently greater in the aspirated series.   The more thorough agitation effected by the steady stream of air which bubbled through the suspensions is most probably the cause of the differ-

ences between the two series. For, with limited periodic agitation, without aeration, it was found that lapse of time caused increases in the amounts of unrecovered sulfate. It is quite possible, however, that with progress of time, more and more of the solid-phase $Ca(OH)_2$ passes into colloidal state, by which change its absorptive properties are naturally increased. Both conditions— continued contact of lime with excess of water, and periodic agitations and shorter period of time with continuous agitation—would tend to effect greater dispersion and augmented absorptive properties. Both conditions do effect increased absorption. It therefore appears that change in physical condition of lime suspensions, is the cause for increased calcium sulfate absorption and this change may be induced in the main either by time or agitation.

Experiment 8. Residual effect of $Ca(OH)_2$ upon subsequent additions of soluble sulfate to suspensions of ignited and unignited soil

The data of table 2 show that the large bulks of solid-phase $Ca(OH)_2$ cause an absorption of the sulfate radical, *per se*. The data of table 3 show that, to a minor extent, the mass of acid soil also removes SO_4 from solution. Table 3 and 4 show further that the absorptive property of the soil mass was greatly increased upon the addition of the excess of lime. It appears further, from tables 5 and 6, that the conversion of the excess of $Ca(OH)_2$ into $CaCO_3$ nullified the ability of the soil to retain the sulfate which was added before, or simultaneously with, the introduction of lime. Experiment 8 was accordingly planned to determine the residual effect of $Ca(OH)_2$ upon the retentive activities exerted by soil and its ignited residue for sulfate additions before and after carbonation by means of CO_2. It was thought that dehydration of hydrated siliceous and other materials, conversion of all ferrous and ferric components into ferric oxides, destruction of colloidal complexes and elimination of organic matter, through the agency of intense heat would give some indication of the reasons for the marked increase in a soil's retentive properties for sulfate when it is treated with an excess of $Ca(OH)_2$.

The following conditions were therefore imposed: Constant charges of 500 gm. of soil, or its ignited residue, and 20.0 gm. of high-grade commercial $Ca(OH)_2$ and a constant volume of 2,000 cc. of distilled water were used. The 500-gm. charges of soil were ignited at 900°C. for three hours in a large electric furnace. The soil and residue suspensions and $Ca(OH)_2$ additions were agitated every half hour for seven hours and permitted to stand overnight before the addition of Na_2SO_4 to six of the eight suspensions by means of a 25-cc. volume of an aqueous solution. They were agitated hourly seven times, during the second day, and again permitted to stand overnight. Aliquots of 500 cc. were withdrawn for titrations and $BaSO_4$ determinations. Aqueous extracts of soil and ignited soil were made as controls against the same suspensions plus Na_2SO_4. At the end of the first overnight period CO_2 was passed into one of the soil-$Ca(OH)_2$ suspensions, and one ignited residue until all $Ca(OH)_2$ was converted to $CaCO_3$.

The sulfate recovery from the ignited control was more than twice that obtained from the untreated soil after extraction for 48 hours, and also after 16 days. On the other hand, the two sulfate recoveries from the fortified ignited residue were only 92.3 per cent and 93.5 per cent of the sulfate addition, while those from the Na_2SO_4-soil control were 4 per cent and 6 per cent in excess of the added sulfate. The addition of $Ca(OH)_2$ had a very decided effect upon

TABLE 10

Residual effect of $Ca(OH)_2$* upon subsequent additions of soluble sulfate solution to suspensions of ignited and unignited soil* after periods of 48 hours and 16 days (experiment 8)

AQUEOUS SUSPENSIONS OF	ALKALINITY 500 CC. ALIQUOTS TERMS OF 0.5 NORMALITY AFTER		SULFATE CONTENT OF AQUEOUS EXTRACTIONS, AS BaSO4 EQUIVALENT PER 500 CC. ALIQUOTS					
			After 48 hours†			After 16 days		
				Deviation from respective controls			Deviation from respective controls	
	48 hours	16 days	Found	Found	Basis of Na2SO4 addition	Found	Found	Basis of Na2SO4 addition
	cc.	cc.	gm.	gm.	per cent	gm.	gm.	per cent
Soil....................	0.6	1.6	0.1005	....	....	0.1075	....	....
Ignited soil..............	0.8	1.0	0.2234	0.1229	....	0.2176	0.1101	....
Soil plus Na2SO4..........	0.6	1.5	0.3705	0.2700	104.0	0.3830	0.2755	106.1
Ignited Soil plus Na2SO4....	0.8	1.0	0.4630	0.2396	92.3	0.4603	0.2427	93.5
Soil, Na2SO4 and Ca(OH)2..	37.4	33.5	0.1405	−0.2300	−88.6	0.0183	−0.2647	−102.2
Ignited soil, Na2SO4 and Ca(OH)2..............	37.4	19.7	0.0832	−0.3798	−146.3	0.0033	−0.4570	−176.0
Soil, Na2SO4, Ca(OH)2 plus CO2...................	4.4	‡	0.3130	−0.0575	−22.2	0.4215	0.0385	14.8
Ignited soil, Na2SO4, Ca(OH)2 plus CO2	9.9	2.8	0.4145	−0.0485	−18.7	0.4987	0.0384	14.8

* 20 gms. commercial hydrate to 500 gm. of soil in 2,025 cc. distilled water.

† Na2SO4 additions equivalent to 0.2596 gm. BaSO4 per 500 cc. aliquot made 24 hours after making suspensions and immediately after conversion of excess of $Ca(OH)_2$ into $CaCO_3$.

‡ Uncertain endpoint because of instability of indicator in colored supernatant.

the removal of sulfate from solution in both soil and ignited-residue suspensions, the effect increasing with time. The differences between the recoveries from the fortified-soil suspension and those from the 3-component suspension, soil-Na_2SO_4-lime, showed removals of 88.6 per cent and 102.0 per cent of the sulfate addition from solution phase, as a result of the influence exerted by the lime during the two periods. But the absorption exerted by the ignited residue and lime suspension was still more extensive for both periods, amounting, respectively, to nearly 1.5 times and over 1.75 times the amount added as Na_2SO_4. The 48-hour and 16-day sulfate extraction from the suspension of ignited

residue, plus both Na_2SO_4 and lime, were, respectively, only 82.8 per cent and 3.1 per cent of corresponding recoveries from soil alone, and only 37.2 per cent and 1.5 per cent of corresponding extractions from the unfortified ignited soil. The sum of aliquot recovery from the ignited residue treated with Na_2SO_4 and $Ca(OH)_2$ and the aliquot fraction of added sodium sulfate was 0.1302 gm. less than the recovery from the ignited residue treated with sulfate without lime for the 48-hours period. For the 16-day period a corresponding discrepancy of 0.1974 gm. was obtained. With continued contact of ignited residue plus Na_2SO_4 with excess of lime the sulfate recovery was practically nil. It is thus apparent from the 48-hour-contact data that after the changes incident to burning, the added lime was responsible for completely removing from the solution phase not only all of the added sulfate, but also 0.1202 gm. of that dissolved from the original unlimed ignited residue by each 500-cc. aliquot. But the 16-day period served to eliminate all but 0.0033 gm. of the 500-cc. aliquot total of 0.5889 gm. supplied by ignited soil, $Ca(OH)_2$ content, and Na_2SO_4 addition.

Inspection of the soil-sulfate-lime suspension showed it to be very different from the corresponding ignited-residue suspension. A part of the ignited soil had been converted to coarse red granules, undisintegrated by the subsequent suspension and agitation. But the more granular part was capped by a large amount of a reddish flocculant interspersed throughout the lighter upper zone of lime, while no such occurrence was noted in the soil suspensions. After several days contact and settling overnight following agitation, the unignited soil plus sulfate and lime had a depth of 1.87 inches in the 4-liter bottles, while the ignited residue containing sulfate and lime was 2.87 inches deep. It will be noted also that though both soil and ignited residue suspensions decreased the $Ca(OH)_2$ concentrations in the interval of fourteen days, the ignited soil was very much more effective in this respect.

The passage of CO_2 into admixtures of sulfate and lime, with soil and with ignited soil, caused a decided difference in the amounts of sulfate held by the two solids against the 48-hour extraction. The recovery from the soil fortified with Na_2SO_4 was 2.25 times that from soil with the same sulfate addition plus lime. But the recovery from the fortified ignited residue was five times that obtained from the same residue in contact with $Ca(OH)_2$. In spite of a still further addition of sulfate through introduction of the sulfate impurities of the calcium hydrate, the recoveries from the two carbonated media after forty-eight hours were not so great however as those obtained from the respective controls fortified with Na_2SO_4 in the absence of lime. The residual effect of the added hydrate still appears to be in some evidence, therefore, at the conclusion of the first period of contact. This residual effect had disappeared entirely, however, after fourteen days for both soil and ignited residue, each of which gave recoveries about 15 per cent above the respective controls.

The characteristic flocculation and color of soil mass, mentioned in discussing the ignited residue suspensions containing Na_2SO_4 and $Ca(OH)_2$,

disappeared entirely after conversion of hydrate to carbonate. Likewise the depth of the columns were the same, 1.62 inches, as compared to depths of 1.87 inches and 2.87 inches, for soil and ignited soil, prior to the passage of CO_2.

The readiness with which the ignited iron underwent hydration and flocculation in the $Ca(OH)_2$ solutions was most striking. The distinct increase in retentive power of the soil after ignition, coincident with the presence of the mass of hydrated iron oxide, the rapid precipitation of the iron upon treatment with CO_2, and the coincidental loss of absorptive power suggest rather forcibly that the hydrating effect exerted by $Ca(OH)_2$ upon ferric and probably aluminic compounds in the soil is one, if not the main, cause for the retention of soluble sulfates by the soil mass. Silica and silicate complexes also may have been of some effect. Further work is planned to determine more fully the extent to which iron, alumina and silica may be, singly or jointly, responsible for the observed absorption phenomena.

CHANGE IN $Ca(OH)_2$ CONCENTRATION AS INFLUENCED BY SUSPENSIONS AND BY TIME

Both soil and ignited-soil controls, and the same controls plus Na_2SO_4, gave somewhat greater alkalinity indications in the 500 cc. aliquots after sixteen days. The reverse was true, however, for the lime additions to both soil and ignited residue. While the decrease in alkalinity was very positive in the soil suspension it was still more impressive—equivalent to 47.3 per cent—in the ignited residue suspension. A titration made nineteen days later showed a still further decrease to 30.2 per cent of that found after the first 48-hour contact. The decrease in $Ca(OH)_2$ could hardly be attributed to continued reaction between insoluble acid components of the soil and $Ca(OH)_2$ during the 48-hour preliminary period. In the ignited residue, eradication of acid reacting materials was still more positive. However, the ignited residue was still more effective in decreasing the $Ca(OH)_2$ concentrations in the aqueous suspensions. Corresponding data in tables 3 and 4 show that with increase of time there is a definite decrease in $Ca(OH)_2$ concentrations of the aqueous extractions from similar soil suspensions. It is apparent therefore that the $Ca(OH)_2$ exerts a progressive hydrating action upon soil. The hydration of the ignited residue was still greater. The products of the hydrating action have the property of absorbing $Ca(OH)_2$ as well as $CaSO_4$. With marked increase in absorptive properties, there was readily discernible a considerable increase in hydrated Fe_2O_3 which resulted from contact of $Ca(OH)_2$ with the ignited residue. From this it would appear that the hydrated iron oxide was responsible, in part at least, for progressive adsorption of $Ca(OH)_2$.

FURTHER SULFATE RECOVERIES FROM RED FLOCCULATE OF IGNITED SOIL AND LIME SUSPENSIONS

Since the preparation of this manuscript and its approval for publication a contribution by Lichtenwalner, Flenner and Gordon (4) has thrown considerable

light upon the problem more especially the findings of tables 10 and 11. These investigators found a definite adsorption of the $CaSO_4$ molecule by ferric and aluminic hydrogels obtained by ammoniacal precipitations. It was also found that some of the adsorbed SO_4 radical could be recovered by successive aqueous extractions.

Nineteen days after the end of the 16-day period of contact given in table 10, a 600-cc. volume of the supernatant and upper part of the suspension of the fortified ignited residue and $Ca(OH)_2$ was syphoned off into a 600 cc. cylinder. After settling, the upper 550 cc. of $Ca(OH)_2$ solution and suspension was withdrawn and the lower 50 cc. discarded. Of this 550-cc. volume, the upper 365-cc. portion was clear $Ca(OH)_2$ solution and the lower 185-cc. fraction was reddish lime-impregnated flocculate. The flocculate was thrown upon a

TABLE 11

Additional sulfate recoveries and alkalinity determinations from a portion of the ignited-residue-lime suspension fortified with Na_2SO_4

LAPSE SINCE PREVIOUS EXTRACTION	0.5 N VALUE PER 500 CC. EXTRACT	BaSO₄ PER 500 CC. EXTRACT
	cc.	*gm.*
19 days	11.3* †	0.0473* ‡
2 hours	5.3	0.0293
2 hours	4.5	0.0260
1.25 hours	4.5	0.0259
1.50 hours	3.5	0.0240
Overnight	4.6	0.0286
1.50 hours	3.9	0.0232
1.25 hours	4.0	0.0202
2.50 hours	˙3.6	0.0210
Overnight	4.0	0.0295
	49.2	0.2730

Residual sulfate in flocculate obtained by Na_2CO_3 fusion 0.3690 gm.

* Calculated from determination on 550 cc. volume, inclusive of flocculate.

† Corresponding determinations 35 days previous 19.7 cc., 37 days previous 37.4 cc.

‡ Corresponding determinations 35 days previous 0.0033 gm., 37 days previous 0.0832 gm.

Büchner filter and washed with 100 cc. of distilled water. The residue was then returned to the stoppered cylinder and subjected to the successive extractions and determinations specified in table 11.

The reddish flocculate was analyzed after the tenth extraction shown in table 11. The entire flocculate weighed 36.9155 gm. Of this, 2.4610 gm., or 6.67 per cent, was accounted for by CaO; 2.3060 gm., or 6.25 per cent, was due to strong-HCl soluble Fe_2O_3-Al_2O_3-P_2O_5 and 26.4093 gm., or 71.54 per cent, was SiO_2. There was therefore about 15 per cent of acid insoluble Fe_2O_3-Al_2O_3 in the more inactive granules. Of the total SO_4 present from $Ca(OH)_2$ impurities and Na_2SO_4 addition in the full residue after ignition of soil, 0.0865 gm. had been removed by the two extractions shown in table 10. There was left, therefore, 1.8751 gm. in the entire charge accounted for by ignited residue and Na_2SO_4

and disregarding SO_4 impurities in the full charge of lime before the two extractions of table 10.   Including the sulfate impurities, there was an initial sulfate occurrence of 2.2138 gm. $BaSO_4$ equivalence.   At the beginning of the ten extractions of table 11 the $BaSO_4$ equivalence present was therefore 2.1273 gm.   The sulfates unrecovered by the aqueous extracts impregnated with $Ca(OH)_2$ gave a $BaSO_4$ equivalence of 0.3690 gm.   Of the amount present a total $BaSO_4$ equivalence of 0.6420 gm., or 30.1 per cent, was found in the more hydrous flocculate suspended in 185 cc. volume of $Ca(OH)_2$ solution.   The 0.3690 gm. residue after the extractions was 1.35 times more than the total amount recovered by the ten successive aqueous extractions.   The total bulk of lime and insoluble residue, including the portion subjected to the ten additional aqueous extractions, amounted to 715 cc.   The unextracted 530-cc. portions contained most of the granular oxides and lime and it was much more compact than the upper 185 cc. used in obtaining the ten extractions of table 11.   It did, however, contain a considerable quantity of the more flocculant material which furnished the 185 cc. volume of successively extracted flocculate.   It is thus apparent that 30 per cent of the sulfate was occluded by the reddish flocculate made up of $Ca(OH)_2$ and hydrated oxides of iron and aluminum and silica, which represented 25 per cent of the bulk of the suspension as it stood in the cylinder.   Upon filtration, however, the flocculate was compacted to a volume of about 35 cc.   On the other hand, the more granular fraction was changed but little in bulk by filtration.   It is not established what part of the determined sulfate adsorption is to be attributed to either of these several components.

EXPERIMENT 9.   INFLUENCE OF $Ca(OH)_2$ UPON RAIN WATER CONCENTRATIONS
OF SULFATES

In the report of previous lysimeter experiments (7, 8) it was pointed out that the leachings from the heavily limed tanks were of lower SO_4 concentration than the same waters prior to their movement through the surface soil.   Since the sulfate concentrations of rain water were much less than those of the several sulfate solutions used in the present experiment, it seemed desirable to impose some of the previous contact conditions with rainfall concentration of sulfates. Accordingly, the lime treatments were made to rain water alone and to rain water and soil.   As controls, $BaSO_4$ determinations were made upon rain water, distilled-water extractions of $Ca(OH)_2$, and rain water extractions of soil alone. Five hundred grams of soil, 23.22 gms. of high grade commercial lime, and 3500 cc. of rain water were used.   The lime charge carried 0.3910 gm. of $BaSO_4$ equivalent.   The containers were agitated several times during the afternoon when charges were introduced.   After standing overnight undisturbed, they were agitated hourly for seven hours during the following day and again permitted to stand overnight, after which 1-liter aliquots were withdrawn for titrations and $BaSO_4$ determinations.   The residues were then permitted to

stand for fourteen days, being agitated once each day during that interval. The results obtained from the five conditions named are given for both periods of contact in table 12.

By subtraction of the amount of $BaSO_4$ found in one liter of rain water from the rain water extract of the burnt lime, a gain of 0.0780 gm. appears for the 36-hour contact. This increase fell 0.0337 gm., or 26.2 per cent, below the computed total amount present. The 0.0817-gm. recovery from the burnt lime by the parallel distilled-water extraction amounted to 73.1 per cent of that present, or a discrepancy of 26.9 per cent. This agrees closely with the corresponding deficiency obtained in the rain-water extraction, although there was an appreciable difference between the $Ca(OH)_2$ concentration of the two solutions. The corresponding data for the 16-day interval showed but little

TABLE 12

Influence of $Ca(OH)_2$* upon the sulfate concentration of rain water alone and with soil† suspensions (experiment 9)

AQUEOUS SUSPENSIONS	ALKALINITY OF 1,000 CC. ALIQUOTS, TERMS OF 0.5 NORMALITY AFTER		SULFATE CONTENT OF RAIN WATER EXTRACTS AS BaSO₄ EQUIVALENT PER LITER‡					
			After 36 hours			After 16 days		
			Found	Variation from		Found	Variation from	
	36 hours	16 days		Actual	Theoretical		Actual	Theoretical
	cc.	*cc.*	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*
Rain water only............	0.6	0.6	0.0168	....	....	0.0168	....	....
Rain water and lime.......	89.6	90.6	0.0948	0.0780	−0.0337	0.1031	0.0863	−0.0254
Distilled water and lime...	88.7	89.4	0.0817	−0.0131	−0.0468	0.0881	−0.0150	−0.0404
Rain water and soil........	0.6	1.9	0.1625	....	....	0.2005	....	....
Rain water, soil and lime..	81.0	72.8	0.0317	−0.1308	−0.2425	0.0238	−0.1767	−0.2884

* 20 gm. CaO per 3500 cc.

† 500 gm.

‡ $BaSO_4$ per liter on basis of total SO_4 content of lime charge, 0.1117 gm.

variation from those of the shorter period. For the 36-hour and 16-day intervals the rain-water extractions of soil alone contained, respectively, nearly ten times and about twelve times the sulfate content of the rain water. These proportions are many times the reverse of the proportion which obtained when rainfall leached through this same soil in the lysimeters. The addition of hydrated lime to the rain water and soil caused a decrease of 80.5 per cent from the recovery obtained in the absence of lime after 36 hours, or a decrease of 81.1 per cent of the theoretical, as represented by the sum of the soil extraction and the amount which would have been present in 1 liter if all SO_4 had been dissolved from the lime charge. The corresponding differences obtained after 16 days were still greater. The discrepancy between the depressive effect

exerted by the excesses of lime upon the rain water during its passage through the limed surface soil and the corresponding effect upon the rain-water extractions is most probably due to the better opportunity afforded for solution of the sulfate impurities of the lime under the imposed laboratory conditions.

COMPARISON OF EXTRACTIONS AND NATURAL LEACHINGS AS MEANS OF SULFATE RECOVERIES

Since the soil used in the sulfate extractions was also used in the 5-year lysimeter studies (7) of sulfate outgo from surface soil alone, an unusual opportunity is afforded for quantitative comparisons between the imposed conditions of agitation and extraction by the large proportion of water to soil and natural leachings from lysimeters.   In so far as we are aware, this comparison has not been made.   One possible vitiating factor in the comparison is that the moist soil was brought to an air-dry condition and maintained in that state during a 5-year interval.   It is possible that such a maintained change may effect the colloidal material of the soil and thus influence its retentive properties. Assuming such to be the case, however, it is quite possible that the agitation of soil with the large proportion of water would quickly cause reversion of the colloidal material to the condition which obtained prior to its being brought to the air-dry state.

The sulfate precipitation per acre surface during the 5-year interval amounted to 214.7 pounds of S.   The soil leachings from the 256.0-acre-inch precipitation during that period would therefore have had for its leaching content 214.7 pounds of sulfur—if the rainfall concentration of sulfates were not altered by passage through the layer of soil—in addition to the amount of sulfate derived from a total soil sulfur content of 0.0326 (SO_3, 0.0815) per cent.   But the average $BaSO_4$ equivalence of 0.0394 gm. per liter (8) in the total 5-year leachings of 716.4 liters from the untreated control tank gave a total sulfate sulfur outgo of only 175.8 pounds, or 38.9 pounds less than the sulfur brought to the soil by rain water during the same period.   As against this outgo in the lysimeter leachings, the 0.1005-gm. $BaSO_4$ determination (table 10) represents one-fourth the water-soluble sulfate extracted from 500 gm. of soil which had been kept in air-dry conditon for nearly six years.   This recovery of 0.4020 gm. $BaSO_4$ (0.0551 gm. S) from 500 gm. of soil is equivalent to 0.011 per cent, or 220 pounds of sulfate sulfur per 2,000,000 pounds of soil.   Thus, by a 48-hour contact, with periodic agitation and extraction a 0.0326 per cent total sulfur content yielded sulfates at the rate of 220 pounds of sulfur per 2,000,000 pounds of soil.   But from the same sulfur content, plus 214.7 pounds of rain-water sulfate sulfur, the 5-year leachings totaled only 175.8 pounds.   There is thus a difference of 44.2 pounds in favor of the aqueous extractions, which demonstrates the intensity of laboratory extractions—for sulfates from this loam, at least—as compared to natural leachings.

A parallel may also be made between the recovery of SO_4 from $FeSO_4$ additions in the laboratory extractions and the sulfate sulfur leached from the same

soil in the lysimeters.   In both cases the sulfate addition supplied S at the rate of 1000 pounds per 2,000,000 pounds of soil.   In both cases, also, the Fe of the FeSO₄ was retained by the soil.   In the extractions, the sulfate recovery was in the form of CaSO₄, while in the lysimeter leachings it was accounted for in most part by native calcium and also by magnesium.   In the unsupplemented FeSO₄ tank, the 1000-pound sulfate sulfur addition yielded 934.6 pounds (8), or 758.8 pounds more than the outgo from the no-treatment tank, during the 5-year period of rainfall leaching.   Of this 5-year total recovery of 934.6 pounds, 534.3 pounds were leached by the subnormal precipitation of 37.69 inches during the first year.   The leachings for the succeeding 4 years were 180.9 pounds, 109.3 pounds, 67.7 pounds, and 42.4 pounds.   From the corresponding FeSO₄-solution-additions the 0.2350 gm. BaSO₄ equivalent, obtained in the 500-cc. aliquot after 24-hours extractions of 500 gm. of soil with 2,000 cc. of water, was 0.0300 gm. less than the amount added.   This extraction-recovery represents 886.8 pounds per 2,000,000 pounds of soil, or practically the same recovery, 892.2 pounds, obtained during the first four years in the lysimeter leachings.   It should be remembered, however, that the lysimeters received as a result of the 4-year composite of rainfall, 175.8 pounds of soluble sulfate-sulfur in excess of that added to the laboratory-extracted suspensions.

It is thus apparent that though dissolved FeSO₄ and CaSO₄ additions were not fully recovered from the acid-soil suspensions by the short-period extractions with periodic agitations, such laboratory treatments were much more intense than natural leachings in the recovery of added soluble sulfates, since the laboratory extractions proved equivalent to four years' leaching in the exposed tanks.

SUMMARY

A study was directed toward the influence of Ca(OH)₂ in causing the soil to retain more of native and engendered sulfates and added FeSO₄.

Preliminary determinations, with wide range in charges, showed a near-constant proportion of total sulfates in HCl solutions of charges (table 1), and a distinctly decreased recovery of water-soluble sulfate impurities, with increase of solid-phase Ca(OH)₂ (table 2).

In equivalence to an 8-ton CaO admixture per 2,000,000 pounds of soil, immediate additions of Ca(OH)₂ to aqueous FeSO₄-soil suspensions gave decreasing alkalinity and increasing sulfate recoveries for 24-hour, 48-hour, and 16-day intervals of periodic agitation, the recoveries after the two longer periods having been in excess of total additions.   With increase of time, the clear supernatant solutions from 32- and 100-ton additions of CaO showed some decrease in Ca(OH)₂ concentration and almost complete absence of sulfates (experiment 1, table 3).

The same findings were obtained when the lime additions were not made until after a preliminary period of contact between acid soil and added FeSO₄ solution.   (Experiment 2, table 4).

After one hour's preliminary agitated contact of soil and $FeSO_4$, the three lime additions were made to sulfates and suspensions agitated hourly for seven hours and left overnight. Sulfates were then determined in the supernatant lime-water solutions and the $Ca(OH)_2$ suspensions converted to $CaCO_3$ by addition of Na_2CO_3. After twenty-four hours, the 8- and 32-ton additions gave sulfate recoveries in excess of the amounts introduced as water-soluble sulfates, while a large increase was obtained also in the 100-ton addition. Fourteen days later the recoveries from all three treatments were still greater, and in excess of added soluble sulfate for all three rates (experiment 3, table 5).

A similar result from conversion of $Ca(OH)_2$ to $CaCO_3$ by means of CO_2 showed the increase in SO_4 recoveries to be due to conditions induced by the presence of $Ca(OH)_2$, rather than to NaOH derived from the $Ca(OH)_2 +$ $Na_2CO_3 \rightarrow CaCO_3 + NaOH$ reaction.

Delay of twenty-four hours in the conversion of $Ca(OH)_2$ to $CaCO_3$, by means of Na_2CO_3, showed the same eradication of the precipitative properties caused by $Ca(OH)_2$, and a similar gain in sulfate recoveries, with increase of time after the $CaCO_3$ conversion, which obtained with the shorter period of $Ca(OH)_2$ contact and its earlier conversion to $CaCO_3$ (experiment 4, table 6).

Additions of dissolved $CaSO_4$ were made to similar soil and no-soil suspensions and five excesses of $Ca(OH)_2$ as parallel to the introduction of $CaSO_4$ through the $FeSO_4$-$Ca(OH)_2$ reaction. The addition of the soil caused a marked decrease in dissolved sulfate. The minimum deviation of -15.8 per cent from addition and water-soluble impurities came from the 8-ton CaO treatment, and the maximum of -97.3 per cent from 100 tons (experiment 5, table 7).

In parallel with lysimeter experiments, where equivalent amounts of $Ca(OH)_2$, $CaCO_3$, MgO, and $MgCO_3$ were used, these four materials were added at 8-, 32- and 100-ton rates in $FeSO_4$ solutions, with and without soil. Concordant SO_4 recoveries from the $FeSO_4$ constant and impurity variables were obtained from $Ca(OH)_2$ alone; but the addition of soil showed decrease parallel with increase in $Ca(OH)_2$. A near-constant recovery from the three $CaCO_3$ additions was changed to increase with treatment in the presence of the added soil. A progressive decrease was found in the $FeSO_4$-MgO suspensions, coincident with increased amounts of MgO. This effect disappeared in the $FeSO_4$-MgO-soil suspensions. Proportionate sulfate impurity recoveries from the three charges of MgO without sulfate additions showed the effect of oxide to be upon the added sulfate. $MgCO_3$, alone and with soil, gave increased SO_4 recoveries parallel with increase in the amount of carbonate additions (experiment 6, table 8).

Agitation of six aqueous $FeSO_4$-$Ca(OH)_2$ suspensions, three with periodic agitation and no aeration, and three with constant agitation induced by an aerating current, showed progressive increase in the amounts of sulfates unrecovered for increase in lime charges under both conditions. Each aerated charge showed, however, less sulfate recovery than that shown by its corre-

sponding unaerated parallel. The foregoing result was considered as due to the more favorable conditions for colloidal dispersion and consequent increased absorption by the excesses of $Ca(OH)_2$ rather than to absorptive properties of the small amount of $Fe_2O_3 \cdot nH_2O$ formed from the ferrous sulfate. It was observed that the yellow color caused by such $Fe_2O_3 \cdot nH_2O$ disappeared entirely upon standing. Possible explanations of this phenomenon are advanced (experiment 7, table 9).

Influence of soil structure, or composition, and the occurrence of hydrated ferric and aluminic oxides and silica as causative factors in the absorption of sulfates by the soil during persistence of $Ca(OH)_2$, were considered for two periods in parallels, between soil and soil-Na_2SO_4 suspensions and similar suspensions of ignited soil. After forty-eight hours the unfortified ignited soil gave an SO_4 extraction more than double that of the control. The sulfate recoveries from the fortified control were greater for both periods, however, than those from the fortified ignited residue. The $Ca(OH)_2$ addition was very much more active upon the fortified ignited residue than upon the fortified soil in causing increased absorption and upon formation of $Fe_2O_3 \cdot nH_2O$. Where $Ca(OH)_2$ excesses were converted to $CaCO_3$, both soil and ignited soil lost most of their absorptive properties during the 48-hour period, while all such properties were destroyed during the 16-day period (experiment 8, table 10).

The more flocculant part of the ignited residue suspension was subjected to ten successive aqueous extractions by which continued sulfate recoveries were obtained; but the larger part of adsorbed sulfate was still retained. The more flocculant reddish fraction of the suspension was found to show greater adsorption than the denser fraction.

On continued contact with $Ca(OH)_2$ solutions and excesses of solid phase $Ca(OH)_2$, the soil suspension caused decreased concentration of $Ca(OH)_2$. The same effect was produced with much greater intensity by the ignited soil residues.

Influence of excess of $Ca(OH)_2$ upon rain-water concentrations of sulfate was studied to throw some light upon the paucity of sulfates in the rain-water leachings from the same heavily limed soil in lysimeters. Lime additions to distilled water and rain water gave minus variations from theoretical in both cases after 36-hour and 16-day periods of contact. Soil-$Ca(OH)_2$-rainwater suspensions resulted in still more striking and progressive decreases for the same periods (experiment 9, table 11).

Comparison between sulfate recoveries obtained by agitation and extraction of soil with large proportions of water and those obtained by rainfall leachings showed the extracted sulfates from the air-dried reserve to be in excess of those leached during 4–5 year periods, in spite of the additional soluble sulfate added to the lysimeters by rainfall. This held for both native and added sulfates.

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THE REPLACEMENT OF SOIL POTASSIUM

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In a previous investigation (4) it was observed that finely crushed potassium-bearing rocks in water solutions, treated with manure extract yielded considerable quantities of water-soluble potassium after standing for four months at a temperature of about 25°C. These results were taken as a basis for an experiment in which 500-gm. quantities of soil in quadruplicate were treated with varying amounts of clover hay and medium decomposed manure, and distilled water added for optimum moisture conditions. Two soils of each treatment were sterilized and two were unsterilized. After incubating 10-12 weeks at 25°C. the soils were air dried and water-soluble potassium was determined.

It was found that there was no relation between the carbon dioxide production and the liberation of water-soluble potassium.

The sterilized soils yielded more water-soluble potassium than the soils in which normal biological activities were allowed to take place. Increased applications of organic matter resulted in increased quantities of water-soluble potassium, but the latter increases did not equal the total amount of soluble potassium added in the form of clover hay and manure. This was undoubtedly due to the adsorptive and absorptive powers of the soil which are known to prevent the soluble potassium from going into solution in subsequent water extractions.

A method to determine this absorbed potassium must be developed before the effects of various soil treatments on the liberation of soil potassium can be ascertained quantitatively.

The experiment reported in this paper was planned for that purpose.

The method used involved replacing the exchangeable bases by treatments with neutral salt solutions such as NH_4Cl, $CaCl_2$, etc. This idea is not new. In 1887 Kellner (3) reported that the absorbed potassium of the soil can be replaced completely by repeated leachings with a hot, saturated solution of NH_4Cl, and that only the potassium in solution and in the absorbed form are extracted, that contained in the un-weathered minerals and rocks not being attacked. He further showed by experiments that only soluble and absorbed potassium can be utilized by field peas.

[1] The writer wishes to express his thanks to Dr. P. E. Brown for reading the manuscript.

Very little attention was paid to these important experiments until later. In 1896 Huston and Bartlett (2, p. 91–96) tried a number of solvents for available potassium and phosphorus. As a result of their investigations they came to the conclusion that alkaline NH₄Cl and neutral NH₄Cl were promising solvents for the determination of available potassium.

Not until 1920 was there any extensive work done on the replacement of soil bases with relation to their availability to plants. Hissink (1) carried on some interesting work on exchangeable bases. He reported that all the absorbed potassium is just as available for plants as that in water-soluble forms, and that only the water-soluble and absorbed potassium is replaced by leaching with solutions of neutral salts, such as NH₄Cl, CaCl₂, etc.

It is thought that the potassium molecule is held adsorptively by the colloidal complexes of the soil. The replacement method involves a reversible chemical reaction on the adsorbed molecules. This reaction stops at the point of equilibrium between the solution applied and that around the colloidal nucleus. It is evident, therefore, that a single treatment with a neutral salt solution will not replace the total amount of absorbed potassium. The leaching process must be resorted to. Due to the relatively small amount of absorbed potassium present in the soil comparatively few leachings are required.

In this experiment it was found that two extractions replaced about 90 per cent of the total absorbed potassium. These quantities being sufficient for the purpose of this investigation no further leachings were made.

Although the processes involved in this work include surface phenomena which are purely adsorptive, the replacement itself is a chemical reaction—limited, however, to the molecules which form the surface layer of a nucleus possessing colloidal properties. Hence, except for the small amount of water-soluble potassium present in the soil, this reaction does not occur in stoichiometric proportions. Neither is it a purely physical phenomenon. Probably both phases enter into the processes, and since that is the case confusion will perhaps be avoided best by using only the term "absorbed" throughout this paper.

<div align="center">EXPERIMENTAL</div>

The Carrington loam samples treated with clover hay and manure described in the previous investigation (4) were used in this experiment. Normal solutions of NH₄Cl or CaCl₂ were first used for replacement purposes. Both solvents were found to give equally good results, but due to the fact that the CaCl₂ extracts contained large quantities of calcium to be precipitated the use of this solvent was discontinued.

One hundred grams of the air-dry soil were placed in shaker bottles with 500 cc. of normal NH₄Cl solution and shaken for three hours in the shaking machine. The soil was allowed to settle and the supernatant liquid was decanted, and filtered through the Chamberland Pasteur filters. Most soils would filter

TABLE 1

Replaceable potassium from soil treated with clover hay and manure

SAMPLE NUMBER	TREATMENT (CALCULATED PER ACRE)					NOT STERILIZED					STERILIZED AND KEPT STERILE				
	Manure	CaCO₃	Ortho-clase	Acid phos-phate	Clover hay	Average K₂PtCl₆	K	K per acre	K per acre added in form of manure and orthoclase	Increase (+) or decrease (−)	Average K₂PtCl₆	K	K per acre	K per acre added in form of manure and orthoclase	Increase (+) or decrease (−)
	tons	tons	tons	pounds	tons	gm.	per cent	pounds	pounds	pounds	gm.	per cent	pounds	pounds	pounds
1	Check (soil in field)					0.0113	0.01819	363.3	0	0	0	0	0	0	0
2	Check (at optimum moisture for 10 wks.)					0.0114	0.01835	367.0	0	0	0.0115	0.01851	370.2	0	0
3	8					0.0168	0.02704	540.8	171.2	+2.6	0.0164	0.02640	528.0	171.2	−13.4
4	16	4	40			0.0219	0.03525	705.1	369.4	−31.3	0.0214	0.03445	689.0	369.4	−50.6
5	32	4	40			0.0335	0.05393	1078.7	711.8	0	0.0362	0.05828	1165.6	711.8	+83.6
6	32	4	40	1000		0.0350	0.05635	1127.0	711.8	+48.2	0.0369	0.05940	1188.1	711.8	+106.1
7	32		40			0.0343	0.05522	1104.4	711.8	+25.6	0.0344	0.05538	1107.6	711.8	+25.6
8			40		4	0.0148	0.02382	476.5	105.4	+4.1	0.0154	0.02479	495.8	105.4	+20.2
9			40		12	0.0198	0.03187	637.5	235.2	+35.3	0.0211	0.03397	679.4	235.2	+74.0
10		4	40		12	0.0189	0.03042	608.5	235.2	+6.3	0.0204	0.03284	656.8	235.2	+51.4
11		4	40	1000	12	0.0194	0.03123	624.6	235.2	+22.4	0.0208	0.03348	669.7	235.2	+64.3

fairly well through filter paper, but some of the sterilized soils in this experiment were too slow in filtering, hence the Chamberland Pasteur filters were used.

The soil residue in the shaker bottles was again treated with 500 cc. of normal NH₄Cl and shaken for three hours. The contents of the bottles were then filtered through the Chamberland Pasteur filters. The filtrates of the two extracts were mixed for quadruplicate analyses of 100 cc. aliquots. The aliquots were heated, made slightly alkaline with ammonium hydroxide, and precipitated with $(NH_4)_2CO_3$. After standing for a few minutes at approximately boiling heat, they were filtered through filter paper and the precipitates washed free from chlorides with hot, distilled water. From this point on the "official" J. Lawrence Smith method for potassium was followed.

The results of the averages of the quadruplicate analyses together with the treatments of the sterile and non-sterile soils, are reported in table 1. The amounts of soluble potassium added in the form of clover hay, manure or orthoclase are given in column 10 of the table. The relation of potassium recovered to the total amount found in the check plus the soluble forms in clover hay, manure, or orthoclase added in the various treatments, is given in column 11. The results are calculated in percentages and also in pounds per acre, one acre representing 2,000,000 pounds of surface soil. The manure used for the treatments contained 1.071 per cent of soluble potassium, the clover hay 0.981 per cent, and the orthoclase 0.0135 per cent.

With the exception of samples 4 and 5 in the non-sterile set, and 3 and 4 in the sterile set, all treatments yielded a decided increase in replaceable potassium. The decreases occurring with sample 4 of both the sterile and non-sterile set cannot be explained here, but the decrease for sample 3 of the sterile set may be due to experimental error.

The clover hay treatments, although applied in smaller quantities, gave better results than the manure treatments. Clover hay seems to be more effective than manure in liberating soil potassium.

The sterile set yielded more replaceable potassium than the non-sterile set. This brings up the question of the possibility of releasing replaceable potassium from the insoluble forms by means of sterilization. This point was cleared up by mixing two 500-gm. portions of air-dry Carrington loam, with 8 gm. of manure (16 tons per acre) and placing in bottles. Distilled water was added to bring the soils to the optimum. One sample was sterilized in the autoclave at 15 pounds pressure, for three hours in six intermittent sterilizations, the intermissions being 36 hours. The soils were then air dried and the replaceable potassium determined in the usual way. The results of quadruplicate determinations reported in table 2 give averages which are alike for sterile and nonsterile soils. Hence, sterilization had no effect on the replaceable soil potassium.

The larger amounts obtained in the sterile set may be due to the action of the decomposition products resulting from the application of heat and pressure on the organic matter.

The increased biological activities, so clearly indicated by the larger amounts of carbon dioxide produced in the previous investigation (4), but which showed no relation to water-soluble potassium, gave no indication of any relationship to the replaceable soil potassium.   The largest increases in replaceable potassium were, with few exceptions, directly related to the largest applications of organic matter.

If the contentions of Kellner (3) and Hissink (1) are correct, namely that only water-soluble and absorbed potassium can be replaced and that both of these forms can be utilized directly by plants, then the increased amounts of replaceable potassium obtained in this experiment are directly due to the

TABLE 2

Replaceable potassium recovered from soil treated with KCl, and from sterilized and unsterilized soils

TREATMENT	WEIGHT OF $K_2Pt\ Cl_6$	AVERAGE $K_2Pt\ Cl_6$	K IN 50 GM. SOIL	K ADDED	K RECOVERED
	gm.	gm.	mgm.	mgm.	per cent
No treatment....................	0.0167 0.0188 0.0169 0.0195	0.0179	14.40	0	0
50 gm. KCl......................	0.0479 0.0466 0.0462 0.0468	0.0469	37.73	26.2	88.9
Not sterilized..................	0.0202 0.0201 0.0215 0.0200	0.0204			
Sterilized..............	0.0211 0.0200 0.0202 0.0204	0.0204			

effect of clover hay and manure.   Furthermore, this method could be used as a reliable means of measuring the available soil potassium.

The increases indicated in table 1 are not very large, but it should not be overlooked that these results represent probably only about 90 per cent of the total replaceable potassium.   This fact was ascertained by weighing four 50-gm. portions of Carrington loam in tumblers.   Distilled water was added to bring the soils to optimum moisture conditions.   Two of the soils received no other treatment, while the remaining two received 50 mgm. of KCl dissolved in the distilled water applied for optimum moisture purposes.   The four samples were allowed to stand for 48 hours.   They were then extracted according to the regular method used in this experiment.

The results of duplicate determinations reported in table 2 show that 88.9 per cent of the potassium applied was recovered in the two extracts. This fact may be used as a fair basis for estimating the results of the clover hay and manure treated soils. The gains shown in table 1 would increase considerably if calculated on a 100 per cent basis, and would surely be of practical value in farm practice.

CONCLUSIONS

The determination of replaceable potassium in sterile and non-sterile Carrington loam treated with varying applications of clover hay and manure lead to the following conclusions:

1. About 90 per cent of the absorbed potassium of Carrington loam was replaced by two extractions with normal NH_4Cl.

2. The application of organic matter, such as clover hay and manure, resulted in the liberation of considerable quantities of replaceable potassium from the soil. This liberation was increased proportionally to the increased amounts of organic matter applied.

3. The clover hay seemed to effect the liberation of replaceable potassium in a greater degree than the manure. This was observed in both the sterile and non-sterile soils.

4. The carbon dioxide production and the biological activities showed no relation to the liberation of replaceable potassium.

5. Sterilization had no effect on the replaceable potassium, but the sterilized soils, due probably to the effect of the decomposition products resulting from the application of heat and pressure to the moist organic matter, liberated more soluble potassium than the un-sterilized soils.

6. The liberation of replaceable potassium appeared to be largely a chemical process which seemed to proceed in the absence of biological factors.

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THE EFFECT OF AERATION UPON THE DEVELOPMENT OF BARLEY IN A HEAVY CLAY SOIL[1]

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In studies recently carried out in the laboratories at this station upon the deflocculating effect of fertilizer salts, one of the points that has been particularly emphasized in the relation of this tendency to plant growth is the effect of an increase in aeration or oxygen supply in the substratum. The marked response of the plants studied in artificial culture (1, 2) to the aeration of the substratum made it desirable to investigate the same relation in the soil. Results should directly aid the study of cultural or fertilizer practices which tend to render the soil mass more compact and less pervious to the ready movement of both air and water.

After a ten year period of experimentation, Lipman and Blair (5), found that, within certain limits the dilution of a heavy loam with sand gives a consistent increase in crop production due, without doubt, to superior aeration. Considerable other data upon the fundamental importance of soil aeration are available. Thus, Howard (4) dealing extensively with the pathogenic side of the question indicates the important bearing of aeration upon certain pathological conditions commonly found among the agricultural plants of that section.

In the present studies with soils the treatments were made according to the same scheme as was earlier used in solution cultures (2). Accordingly, it was found necessary to devise a method whereby solution could be kept in continuous passage through the soil substratum of the cultures so treated. A further treatment was added, by which the soil was kept near saturation all the time. This condition was quite comparable, in point of moisture content, to those cultures receiving the constant flow of solution. The treatment of each series is as shown in table on following page. In these studies all cultures were in the same type of vessels whether receiving aeration or the constant flow of solution through the substratum or not.

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SERIES NUMBER	CULTURE	TREATMENT
I	1 and 2	Simple soil cultures (60 per cent moisture)
II	3 and 4	With percolation and direct aeration
III	5 and 6	As I, with direct aeration alone
IV	7 and 8	Percolation alone
V	9 and 10	Simple soil cultures (90 per cent moisture)

Since the procedure involving the percolation of solution through a soil substratum in the presence of growing plants was found to be so readily carried out, it is thought that the possibilities of this method may extend much farther than its usefulness as a method of aeration. Since the volume of solution passed daily through the soil represents several times the normal amount of that contained in the soil, it is thought that this percolate represents the elusive soil solution to which the plant has access as faithfully as that obtained by any other method known. It would seem, therefore, that studies of its changes may indicate, in a reliable manner, the fundamental physical and chemical changes in the complex plant-soil solution system that are known to accompany plant growth.

It has been found possible to recover by this procedure unusually clear percolates, even from the heavy soil used in the present experiment, although at times, the reaction of the solution was almost neutral.

For the possible usefulness of the method in the study of the interphysico-chemical relations of soil and plant, the procedure will be discussed in some detail before presenting the results of the study in aeration which the method first served.

METHODS

As a culture vessel which might receive a constant flow of solution through a soil substratum and at the same time support growing plants in a normal way, the type of container indicated in figure 1 was adopted. The preparation of the container has been described (2) as used for sand cultures. A large number of such vessels were prepared for these and subsequent studies by cementing together, after first removing the bottoms from all except the smallest, a series of three ordinary, coneshaped clay pots, the largest of which was about 14 cm. in the upper diameter and the smallest 7.5 cm. In cementing the pots together a fairly thin mixture of Portland cement was used. The bottom of the larger was fitted into the top of the smaller consecutively and the bottom of the smallest formed the bottom of the vessel thus constructed.

After thoroughly air-drying, the vessels were heated in a hot air sterilizer for the purpose of removing the hygroscopic moisture preparatory to treating them with hot paraffin both inside and outside while still warm. This treatment prevented loss of salts by impregnation in a fairly satisfactory manner. The opening through the bottom of each percolator was closed by a rubber stopper (B, fig. 1) carrying a short glass tube through which the percolating solution could escape. The upper end of this tube was loosely closed with a small plug of glass wool. In the soil work, a layer of clean sand sufficient to cover the glass wool was placed over this outlet.

The flow of solution into the culture (fig. 1) was controlled by using for the upper arm of the siphon a tube with a bore of ½ mm. In this way about eighteen hours were required for
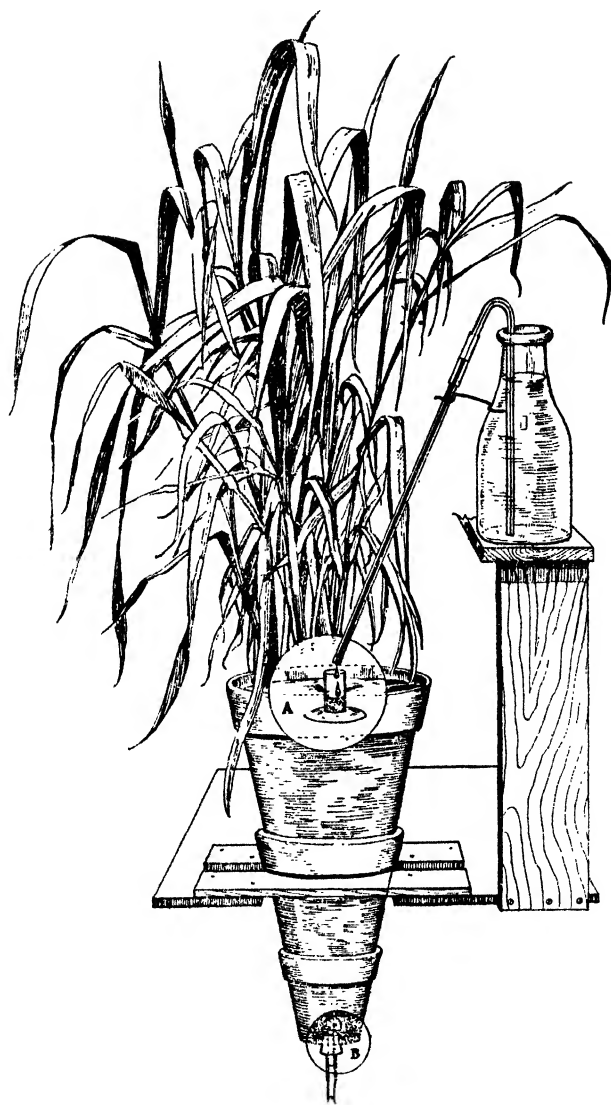
FIG. 1 TYPE AND CONSTRUCTION OF CULTURE VESSEL USED

emptying the bottle. The use of capillary tubing for this purpose has been previously described (2). The rate of flow necessarily decreased with the lowering of the level in the reservoir, but this was regarded as of no great importance since it was only desired that the total flow of one liter through the culture occur within twenty-four hours.

Instead of permitting the solution to drip directly upon the surface of the substratum as in the case of sand cultures, in work with soils a short tube was set upon a watch glass inverted just beneath the surface as indicated in figure 1. Inside the base of the tube a small amount of washed sand was added which sometimes was extended out to the edge of the watch glass as well and thus greatly facilitated percolation by constituting a sort of reservoir which offered a greater surface for diffusion outward and downward into the substratum.

It is to be noted that the lower arm of the siphon was constructed of tubing with an inside bore of 3–4 mm. and thus imposed no great resistance to the flow of the liquid. In the case of alkali soil studies where the rate of flow had to be much slower, the rate was further reduced by bending a loop in the capillary that extended nearly to the bottom of the bottle and thus the total length of that part was increased about two and one-half times.

Perhaps the greatest disadvantage that follows the use of this method in the case of soils is the high moisture content of the substratum which necessarily follows. However the aeration afforded by the practice of passing the solution through the culture daily has been found to correct this as a factor detrimental to plant growth, at least so far as the normality of the root and general development of the plant is concerned. This is indicated by the manner in which the root systems were found to fill the containers in those cultures so treated. In the later cultures with corn the roots were found to penetrate the entire soil mass so thoroughly as to grow out through the lower outlet at B. Excessive moisture in the vessel, which may occur particularly in the case of heavier types of soil, may be satisfactorily controlled by attaching a longer tube to the outlet at B.

STUDIES IN AERATION

Since factors pertaining to aeration of soils will usually be found to be of greatest concern in the heavier types, a heavy Elkton Silt Loam was used in the present study as outlined above. According to the Hilgard method, the maximum water-holding capacity of this soil was slightly in excess of 58 per cent. This type has been defined as consisting of a "grayish silt loam to a depth of about 10 inches which is loose and floury in well cultivated fields but tends to run together when wet and bake upon subsequent exposure." The subsoil is characterized by a grayish color somewhat darker than the surface soil and usually mottled. The type is of marine origin and is derived from deposits that have weathered under conditions of poor drainage.

It is worthy of note that but slight trouble was experienced so far as the permeability of the soil was concerned under the conditions described above to which it was submitted. The percolating solution was found to come through in an exceptionally clear condition throughout the period of the experiment.

Where direct aeration was used pressure was obtained from an improvised air pump previously described (1) and the air bubbled through a trap as shown

attached to the side of vessel 3 in plate 1, figure 2. From this trap the air was conducted to the lower part of the culture vessel and the tube turned upward at about the level of the lower joint, or about two and one-half inches from the bottom. From this point in the lower part of the soil mass a fairly rapid stream of air was passed upward through the substratum.

The vessels were of such size as to conveniently hold 2.6 kilograms of soil. After this amount of soil for each of the ten vessels was properly treated with acid phosphate and placed in the pots, sufficient salts (sodium nitrate and potassium sulfate) were added in the first liter of solution applied to make, in connection with the acid phosphate, the total fertilizer treatment equivalent to a 2000-pound application of a 5-5-5 mixture. Subsequent to this and daily throughout the entire period of the experiment the percolate received in the bottle below was made up to a liter and again passed through the culture. This procedure was thought to produce an aeration effect in the cultures comparable to that of the artificial cultures previously studied in solution and sand. ·

The number and arrangement of the cultures and the treatment of each series are given on page 98. The soil of the cultures receiving 90 per cent moisture, as indicated, was practically saturated all of the time. In the case of those receiving but 60 per cent moisture, the content was more nearly that regarded as optimum for plant growth. The soil of those cultures receiving the repeated flow of solution through the substrata was also found to be very near the saturation point for the greater part of the time. Barley seeds of a beardless variety were germinated and three uniform seedlings placed in each culture on October 2, 1922, and the growth period continued to December 5, in all, 64 days.

The results in terms of average relative dry weights are expressed graphically in figure 2 where relative values in grams are to be found at the foot of the respective columns. Perhaps an even better idea of the effects of the different treatments may be obtained from a study of the plants as shown in plate 1. In these the results of the different treatments are in decided contrast. It is seen that the culture with a high moisture content in the absence of aeration (plate 1, pot 9) gave a considerably lower yield than any of the other treatments. The simple cultures with a substratum having a more normal moisture content followed. The constant flow of solution through the soil of the cultures so treated was found instrumental in effecting a considerable increase in growth over those of the other treatments. But it is apparent that the application of direct aeration is the most effective of all, though there was only a slight difference between the effect of direct aeration alone and its combination with the repeated percolation of solution through the culture. This is quite the opposite of results found in the case of solution cultures discussed previously (2).

Only simple tests of changes in the hydrogen-ion concentration were made from time to time. The reaction of the percolate from cultures receiving the repeated flow of solution was determined at the intervals noted, and the soil

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was tested at the time of harvesting the plants.   For cultures not receiving
the percolation treatment, the soil alone was tested at the intervals noted in
the table.

The results of particular interest in these preliminary data on the change
of reaction of the substratum as a result of plant growth are to be found not
only in the progressive change of reaction of both the soil and the percolate,
but in the marked difference in the extent of these changes.   The change in
reaction of the percolate was found to be considerably greater than in the soil
mass.   This may well raise an important question as to the nature of the
changes which plant growth induces in its relation to the soil and the soil
solution.

Culture No.......	9 and 10	1 and 2	7 and 8	5 and 6	3 and 4
Treatment.......	90 per cent moisture	60 per cent moisture	Constant drip	Direct aeration	Aeration drip
Av. relative dry weight......	100	150.5	193.0	219.5	221.2
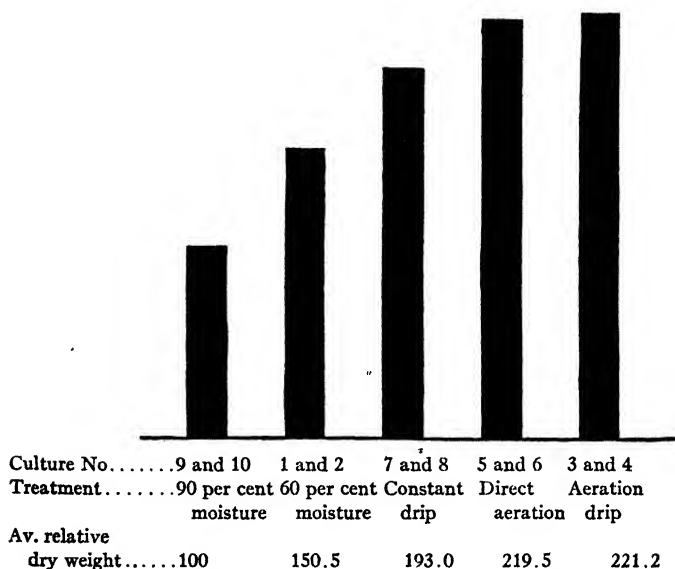
FIG. 2. COMPARATIVE EFFECT OF AERATION AND CONSTANT DRIP UPON THE DEVELOPMENT
(DRY WEIGHT) OF BARLEY T IN A HEAVY CLAY SOIL

It may be well to note, in this connection, that in his studies upon the liming
of humus soils, Odén (6) studied the inverting power of these soils and con-
cluded that this effect, according to the pH values, cannot be accounted for
unless there is a concentration of hydrogen ions around the soil particle greater
than that which expresses the reaction of the general mass of the soil.   This
may be considered in accord with the conclusions of van der Spek (7) when he
notes the greater concentration of hydrogen ions that may be withdrawn to
the soil particles from the soil solution than may be found remaining in the
solution.   He found them to be dislodged from their adsorbed condition by
washing only with difficulty.   In the presence of a rapidly growing crop,

therefore, this greater rate in the change in reaction of the soil solution towards neutrality under the conditions of salt application outlined, might be closely connected both with preferential assimilation of ions or radicals by the plant and the stability of the adsorption to the soil particles of those ions capable of properly counterbalancing this tendency.

Independent of these considerations, the fact which it was hoped to demonstrate by these experiments is the value to the respiratory processes of the plant of a sufficient supply of available oxygen to its roots. The data presented indicate that the response of barley to aeration in a heavy soil was decidedly positive and that any increase of compactness or imperviousness of the soil might well be considered as injurious to plant growth through the consequent decrease in the supply of available oxygen.

Although oxygen determinations were not made upon the percolates, it is of interest to note that in later experiments with a loam soil to which 25 per

TABLE 1

The hydrogen-ion concentration of the soil and percolate at different stages in the development of the barley plants

TIME OF SAMPLING	HYDROGEN-ION CONCENTRATION				
	Cultures 1 and 2	Cultures 3 and 4	Cultures 5 and 6	Cultures 7 and 8	Cultures 9 and 10
	pH	pH	pH	pH	pH
October 2 (2 days)	....	5.5*	....	5.45*	...
October 30 (4 weeks)	5.85	5.9*	6.1	6.15*	5.8
November 27 (8 weeks)	6.05	6.7*	6.25	6.7*	6.0
December 5 (harvest)	....	6.95*	....	6.95*	....
	6.1	6.0	6.0	6.1	6.3

* Value for percolating solution.   All other values are for the soil of the respective cultures as determined in the usual way.

cent clay had been added, the comparative pressures of the gas in the solution of cropped and uncropped pots show that for the latter (fallow) pots the concentration of dissolved oxygen is as much as fourteen times as great as in the percolate of the cropped pots. This particular test was made in the evening after the percolate had flowed through the sampling bottle without coming into contact with the air for an entire day of bright sunshine. In further tests during the night, the differences in the oxygen pressures of the solutions were considerably less marked between the cropped and fallow soils. These studies were conducted during experiments involving the growth of popcorn under the same conditions of culture as those just described for the barley of Series IV in the present studies.

The procedure used in sampling for the determination of oxygen from such soil cultures is the result of an adaptation of the mikro-method of sampling already described (3). In doing this, the tube b of the sampling bottle (3, p. 490) is connected directly with the outlet tube of the percolator. With

the cock c open, the flow of the liquid will fill the bottle and pass out the arm d. In sampling in this manner, considerable difficulty has been experienced in avoiding the entrainment of bubbles of air which emerged from the culture vessel with the slightest exhaustion or evacuation of the system. A precaution that has been found helpful in overcoming this difficulty is to have the outlet d drop only to such a distance that instead of exerting a siphon effect, the opposite condition will prevail and, as a result, a slight pressure will develop in the system involving the arms b and d, the bottle a and the lower part of the percolator.

After a sufficient quantity of the liquid has passed through the sample bottle, the cock c is closed and the procedure in handling and treating the sample in preparing it for titration is the same as has been previously outlined (3).

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PLATE 1

EFFECT OF AERATION ON GROWTH OF BARLEY
R. V. ALLISON
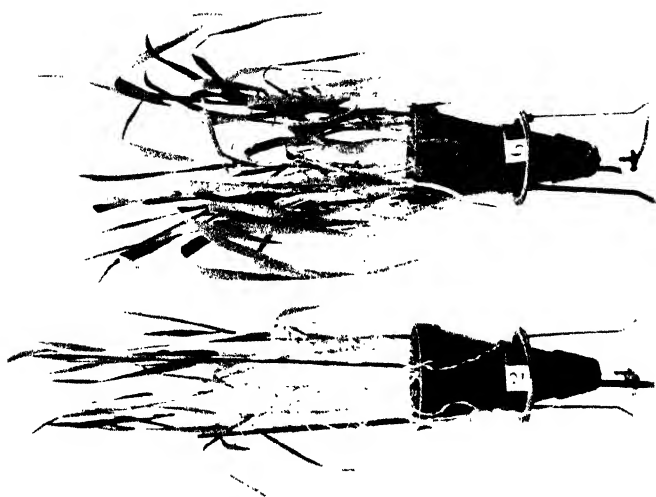
FIG. 1. BARLEY IN HEAVY CLAY SOIL CULTURES

2. Simple culture (moisture 60 per cent)
6. Like 2 with direct aeration
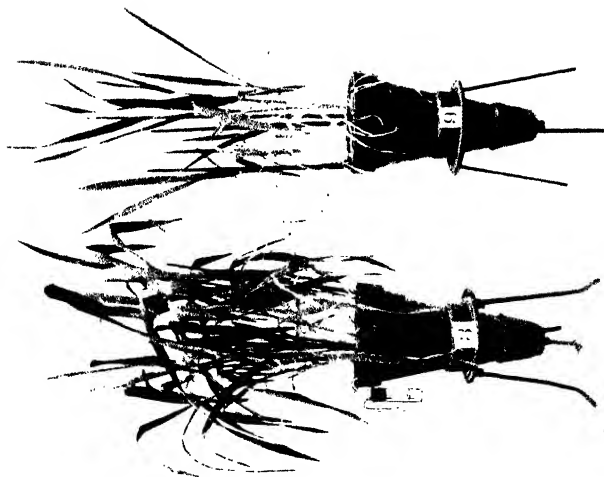
FIG. 2. BARLEY IN HEAVY CLAY SOIL CULTURES

3. Constant drip with direct aeration
9. Not aerated (high moisture, 90 per cent)

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THE STRATIGRAPHIC STUDY OF PEAT DEPOSITS[1,2]

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I. INTRODUCTION

The history and progress of peat investigations have been quite similar to the history and progress of other lines of scientific work. There are first the observations, many of them imperfectly made, then improvements in methods of work and a gradual accumulation of fundamental basic facts, finally the attempts to work out relationships for these facts. If the problems of peatland in the various states individually, or in the United States as a whole is to be solved permanently, and on the right basis, the facts as they exist must be the foundation of that solution.

During the past ten years the writer's primary object of peat investigations in the field has been first of all the collection and study of profile records of peat deposits, irrespective of the use made or the utility to be made of the peatland. The profile records of peat deposits have contributed the fundamental facts regarding the three principal groups of peat layers which, because of their immediate practical usefulness, are now occupying the interest of soil survey workers. The peat profiles brought out not only the natural units and divisions of peat materials included in the whole profile, but they have shown also the intrinsic characteristics of the horizons in the surface layers of drained peatlands upon which soil-forming processes have operated. Surface horizons in peat layers are very recent, practically being equivalent to the formation of muck and humus. The profile records, moreover, in their geographic relations have thrown a great deal of light upon the several kinds or groups of peat deposits, the series of type profiles in each group, and the conditions of their formation. These observations may conceivably lead at some future time to successful methods of selecting peatland. The profiles have brought out two important divisions of peat deposits; namely, (1) those which developed in water basins and under conditions of poor drainage and (2) those which developed on moist flat land under conditions of a

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[1] Read by the author before the Chicago meeting of the American Association of Soil Survey Workers, November 14, 1923. Published by permission of the United States Secretary of Agriculture.

[2] This paper differs in character from those usually published in Soil Science. A special request for its publication has come from members of the American Association of Soil Survey Workers.—EDITOR.

rising or fluctuating water table. The type profiles in the former group of peat deposits show sedimentary layers of peat in the bottom and indicate the need of elaborate drainage measures for reclamation. The type profiles in the latter group of peatland exhibit as initial layers mainly fibrous or woody types of peat; deposits of this group can be readily drained and aerated to the bottom. There is another point in which profile records have been of immediate practical utility. Regarding the most important factors in the accumulation of peat layers, the profile records emphasize on the one hand the influence of the time interval during which various kinds of peat-forming vegetation contributed the number, character, and position of separate layers of plant remains; on the other hand they stress the significance of the limited supply of air. Consequent to the saturation with water, the decomposition of peat layers is prevented. Soil-forming processes can act only as the organic material becomes partially drained or cultivated.

These concepts relating to peat layers and horizons, to profile types of peat deposits, and to factors of peat accumulation have been presented in various publications (1–5). On the basis of these concepts a correlation of the experimental results has been made possible with reference to the profile structure of both American and European peatland. In their present genetic and geographic relationships these concepts are gaining acceptance among men active in field and laboratory peat investigations. Without reference to the practical importance to soil bacteriology and plant nutrition, knowledge of the profile section of peat deposits constitutes a distinct step forward for various lines of scientific work, including ecology, geography, economics, paleontology, and even archaeology. The stratigraphic section of a peat deposit,—the profile as a whole—must be the unit as well as the subject matter for a practical detailed survey, for the classification and mapping of peatland, and for questions of crop production. A consideration of the manner of occurrence, behavior, and adaptability of different layers of peat material at and beneath the surface is essential to the effective and intelligent conduct of agricultural and industrial operations. The location and construction of drainage channels, of roads and buildings on peat deposits, requires in advance information regarding the different layers of peat to be encountered. It is essential to test peat deposits with adequate sampling tools and with reference to layers and horizons, and to reconstruct with some degree of accuracy the main outlines of both surface and underground distribution of peat layers. In order to solve the problems arising from enforced practices such as excavating peat for the preparation of organic fertilizer composts, for sanding and flooding peat areas, or for finding the necessary means to meet undesirable field conditions which contribute to plant diseases, it is important to know and understand the stratification of peat deposits (6, 7). It is obvious also that the economic necessities with respect to qualified settlers and the country's future requirements of potential farmland require a better selection of peat deposits on the basis of structural quality.

Field work on peat deposits has now been effective over a sufficient time and area in this country to warrant the belief that an account of the method for the stratigraphic study of peat deposits may contribute to a better understanding of peat investigations as a field problem. Before proceeding, however, to a detailed description of the field method in use at this time it should be pointed out, in a brief summary, that the most important contribution from a stratigraphic field method consists in the recognition and description of the different layers of peat in the whole peat profile, their number and arrangement relative to one another, their thickness and continuity, the mineral subsoil, and the source of water supply.

In connection with these various criteria the separate horizons are established which have developed, in the surface of drained peatland, through the operation of soil forming processes such as aeration, cultivation, and others. In these cases, the effects and stages in disintegration and decomposition of the original plant material are also considered, and the thickness, texture, structure and color of each of these horizons in the upper part of the peat profile are determined.

The principle and method of differentiating peat deposits into series and type-profiles is based upon the number of peat layers and horizons, and upon a combination of characteristics rather than upon any single ecological, botanical, physical or chemical peculiarity. On the whole, the stratigraphic method of classifying and mapping peatland is essentially the same as that which is now being practiced for mineral soils. To determine the type profile and the proper boundaries of a peat area requires practice in clear visualization of the horizontal and vertical space relations of the different layers exhibited by peat deposits. Actual observations of the whole structure beneath the surface are impossible, however, except by means of soundings and test-holes, supplemented by observation in excavations and ditches. From the nature of things transitions and blending of peat layers cannot always be indicated in a profile record, or sharply drawn on the map; consequently indistinct peat profiles should be expected, making it impracticable, at least at present, to define certain peat areas, or to attempt to draw boundaries for them. Although certain peatlands, mapped under a given number, symbol or type profile by this method, may not always be closely similar to related deposits, yet a sufficiently complete knowledge and classification of that area is thus made possible. Unquestionably the stratigraphic method and its results will serve as a basis for further and better work.

II. CHARACTERISTICS OF THE DIFFERENT GROUPS OF PEAT MATERIAL

In order to identify in the peat profile the units or layers and horizons of organic material it is necessary to have a certain amount of botanical information regarding the plant remains which constitute peat. There are certain genetic relations between various kinds of peat, an elementary knowledge

TABLE 1

Structural units of peat deposits and some of their physical characteristics*

GROUPS OF PEAT-FORMING VEGETATION	TYPES OF PEAT	CHARACTER OF PEAT LAYERS	COLOR OF PEAT LAYERS	TEXTURE OF PEAT LAYERS	STRUCTURE OF PEAT LAYERS
Aquatic	Macerated* Colloidal*	Pulpy (sedimentary)	Olive green, brown to black	Coarse to very finely divided	Compact, impervious, stiff, plastic or loose, friable
Marsh	Reed* Sedge* Brown moss*	Fibrous	Gray, red, or yellow-brown to dark brown	Coarse to fine fibered	Dense, matted, felty, or porous, spongy
Bog	Bog moss* Heath shrub				
Swamp	Willow-alder shrub Deciduous forest Coniferous forest*	Woody	Dark brown to blackish brown	Coarsely fragmented to granular	Compact and granular, or loose, wicker-like

* The characteristics and the physical appearance of the corresponding types of peat marked with an asterisk are among those shown in the illustrations on plates 1–5.

of which is essential to intelligent observation and interpretation. For this reason it may be of value to restate briefly the chief points of interest in the classification of the peat materials previously described (3) and to illustrate the character of some of the layers of peat (table 1 and plates 1–5).

For the convenience of the fieldman, the ten different kinds of peat now known, (their phases and variations run well into a hundred) may be placed into three chief groups; viz., the group of sedimentary layers of peat, the group of fibrous peat, and the group of woody layers of peat. This differentiation is basic and refers roughly to the preponderance of plant constituents and to textural, structural, and certain other characteristics. These features may be supplemented by quantitative measurements, such as water-holding capacity, diffusion of air and gases, conduction of heat, bacterial population, solubility of the organic material, etc. The importance of distinguishing between the three groups of peat layers can not be too strongly emphasized. A separation of this kind is necessary, since field observations have shown that differences in the profile of peat deposits are wide and important.

For general practical purposes, it is sufficient to describe peat materials occurring as layers in terms of composition, texture, structure, and color; this will give the necessary information to form a fairly good idea of the main differences between separate peat layers and to localize their relative position. For purposes of correlation it is desirable however, to classify peat layers more definitely by actually noting the botanical identity of the plant remains present. As potential soils they are not merely the physical support of growing crops; but they also furnish the energy and organic compounds which can be utilized either directly or indirectly by fungi and bacteria, and so be made available for higher plants. These and other peculiarities are very closely correlated to the botanical differences and character of the various layers of peat.

Pulpy peat layers

The most characteristic feature of pulpy peat layers is their sedimentary nature (plate 1 and fig. 2). Residual sediments are formed by the decay of aquatic vegetation; while transported organic sediments, derived from floating mats or various other units of vegetation, have been carried from their source of origin and redistributed usually by water currents, less commonly by wind. A layer of pulpy peat has no visible plane of bedding although the original sediments were laid down in practically horizontal position under conditions differing probably in rate of deposition, seasonal changes, and other causes. The plant remains are relatively small in size; in range of texture they vary from coarse to very finely divided particles, while in structure the layer may be impervious, dense, heavy, stiff and compact. When obtained moist the principal colors of the peat samples are black and dark brown or gray and olive green, with darker shades and variations upon exposure to the air. The material possesses the property of shrinkage to a remarkable degree; it becomes a very hard and hornlike substance upon

drying, and breaks with conchoidal fracture. Sedimentary layers of peat are easily excavated but do not stand in vertical walls. Under heavy loads and in ditches they yield gradually by plastic flow. Under conditions of good drainage pulpy peat has a tendency to break into angular fragments, finally weathering into a fine granular dust.

Pulpy, sedimentary, layers of peat invariably indicate conditions of accumulation below water; they may occur at, near, and below the surface of a peat deposit, in large masses or in comparatively small sheet like beds. The layers may be lenticular, gradually becoming thinner and giving place to overlapping layers of fibrous or woody kinds of peat. A sedimentary inclusion is therefore likely to resemble decomposed phases of surface layers of peat. A horizon of this kind, unless carefully examined microscopically, is often mistaken for the product of layers that are no longer protected by water from oxidation and decay. In penetrating layers of pulpy peat sheets of water may be found above them.

In the pulpy group of peat layers are included the macerated, colloidal, and doppleritic types of peat material. Transition phases may contain an admixture from fibrous or woody plant remains, or varying amounts of shells, chara marl, diatomaceous earth, and of mineral matter such as silt, sand, and clay.

Fibrous peat layers

The outstanding characteristic of fibrous layers of peat is their matted or felt-like porous nature, which has its origin in the interwoven network of more or less unaltered plant remains. The organic constituents are chiefly derived from roots, rootlets, and rhizomes of herbaceous plants and from mosses (plates 1–4 and fig. 2). Fibrous peat occurs in layers owing to the striking differences in the vegetation units themselves which have succeeded one another, and from which the separate units are derived. They differ widely in character. Their physical properties, ease of disintegration and decomposition, as well as various other features, are closely related to the botanical origin of the layers. Commonly the larger portion of a sample volume of fibrous peat consists of pore spaces; and as pores are continuous, layers of fibrous material are a medium in which water salts, or air may move freely. Because of this porosity, fibrous layers can be well drained and aerated and they stand up well in excavations and trenches. In texture, they vary from coarse to very finely fibered material, exhibiting on that account a rather loose, porous appearance. Pulpy peat when present as an admixture acts like a cement in a fibrous layer, making it firm and compact when dry. The colors are variable, ranging from shades of gray, red or yellow brown to dark brown. Contact with the air imparts a darker shade, and admixtures of finely divided organic matter add a very dark brown or black color; mineral salts may lend various shades of yellow, brown and red. Under conditions of slow drainage particles of finely fibered roots oxidize and disintegrate readily

into a black, granular material, but when overdrained they remain more or less unaltered and dry, owing to the high absorption of air.

The individual layers of fibrous peat may be very thin or they may be measured in feet, and accordingly may be described as thin bedded and thick bedded. Although laid down in practically horizontal position a layer of fibrous peat does not necessarily form a continuous stratum. It may occur interbedded or may grade into a layer of woody or of pulpy peat by admixture, or it may give place to overlapping beds of other kinds of fibrous peat material. It is not unusual to find fibrous layers which must be described by terms indicative of mixtures.

The group of fibrous peat layers embraces the "radicellate" reed and sedge types, and the moss types of peat; they are derived from well marked vegetation units which differentiate marshes and bogs.

Woody peat layers

The important feature of woody peat layers is the large amount of woody material from shrubs and trees either as the dominant component or as a prominent admixture in fibrous or finely divided peat material (plate 4, 5 and fig. 2). Owing to the lower water table required by peat-forming shrubs and trees, this group of peat layers is affected by aeration and weathering. The woody plant remains are broken down partly into granular debris and partly into irregular-shaped woody fragments which have escaped or resisted alteration by the decomposing action of air and microörganisms. The depth of the residual weathered debris, and the contact between the decomposing and the more or less unaltered woody material is liable to be extremely uneven, due to the rate of decay under local field conditions. On that account, layers of woody peat may show separate horizons, or an alternation of light brown and very dark brown or black granular organic material, giving the layer a banded or bedded appearance.

Woody peat layers differ widely in composition and character. Their texture, color, ease or difficulty of decay and other properties are more or less closely related to the nature of the plant remains. They may occur at various levels at and below the present surface of a peat deposit and may vary in thickness and continuity.

In the group of woody peat layers are included the types of peat derived from heath shrubs, from willow and alder shrubs, and from deciduous and coniferous forests.

Muck and humus

To the three characteristic groups of peat layers there should be added perhaps a fourth group to include muck and humus and those mineralized phases which are important members of the Clyde, Dunning, and other series of mineral soils containing a large percentage of organic matter. Much work is needed to supply the true facts concerning muck and humus, and

to determine their relation to soil problems. In the opinion of the writer both muck and humus represent approximately a measure of soil-forming processes to which drained surface layers of peat have been subjected. Muck and humus indicate stages of which the former is related to disintegration and the latter is the result of decomposition.

Disintegration is essentially a mechanical soil-forming process by which peat materials are broken into separate and smaller fragments of their constituent plant remains. In places a complete gradation may be seen from the very finely divided material that forms on a cultivated peat soil through various phases of disintegration to the well-preserved, unaltered layers of fibrous or woody peat below. The term disintegration means the physical breaking down of peat at or near the surface. Changes in moisture content, in temperature, more especially the action of freezing and thawing, the growth of plant roots, all play a part in this action. The conditions most favorable to disintegration of peat material are found on drained peat land that lacks the shading and protective covering of a surface vegetation. Peat layers when overdrained have more or less numerous natural partings owing to their irregular drying and shrinkage. The breaks, along which the organic materials separate readily, may be open cracks, or wide open crevices called fissures, and they may occur at intervals of a few inches or of several feet. Cracks and joints afford means of entry to air and soluble salts. Water freezing in cellular plant tissues will burst them causing thin fragments to break off from the parent material. Freezing water in a joint in planes between peat layers or in any crack or crevice exerts the same expansive force that it does in freezing in a pipe; the crack or joint is widened increasingly by each successive freezing and thawing and disintegration operates along and inward the numerous natural breaks. Where crops or native vegetation are growing the rootlets and roots of plants enter the pore spaces and capillaries in the peat material and gradually widen them.

The product of the disintegration of any peat layer is muck. Much of the organic material that has been termed muck is in fact merely the disintegrating drained portion of a peat deposit of which the surface material is in a mechanically divided condition. It may contain varying amount of mineral matter, but the nature and condition of the organic material can be readily determined with the microscope. The sizes of plant fragments may vary in range from the large angular, lumpy pieces of woody debris to the very finely divided particles suspended in the water of the brown, coffee-colored streams of some peat lands. Woody and fibrous peat layers contain more or less abundant fragments of the plant remains that have not been completely broken down. Pulpy, sedimentary layers of peat, on the other hand are less subject to disintegration, since they are themselves on the whole the transported products of disintegration of former water plants or a floating mat of marsh plants, or other vegetation units growing along the shores of water bodies.

Decomposition is a collective term. It includes on the one hand the alterations which plant remains undergo as a source of energy within the drained and aerated or cultivated surface layers of a peatland; and on the other hand it involves the separation from the resistant material of those constituents which are soluble and may nourish crops. The process varies greatly, depending on the position of the ground-water level below the surface. Water soaked layers of peat undergo a very slow partial decomposition because of insufficient oxidation. When a peat layer is drained the plant remains are no longer protected by water from decay and much of the peat material is converted into carbon dioxide. Owing to the loss of the organic matter decomposition produces a great shrinkage of the layer and a proportional increase in the percentage of mineral matter. All peat materials at or near the surface of a drained peat deposit are attacked more or less rapidly by the destructive action of air, changes in temperature and other agencies. The attack on the peat materials is, therefore, mechanical, chemical and biological as well. These three processes are all active, but in any one place a single type of decay may be relatively predominant, owing to the kind of peat material and the field conditions under which the material is decomposed. In every instance, however, some of the more resistant organic constituents are merely broken into smaller fragments (disintegrated); others are changed in their nature (decomposed); while soluble portions remain or go into solution and are carried away. No peat material however resistant can long withstand the normal destructive processes of decay. In decomposition the active agents are air and microörganisms. They destroy peat layers by altering biochemically the constituent plant remains, producing new substances which on the whole are softer, darker in color, and finer in texture than the original parent material. Decomposition is accelerated by factors which are within the control of man; it is favored by manuring and tillage, by warmth and conditions of moderate moisture content. Low temperatures, dry air, or water containing no oxygen have little or no effect on altering and dissolving the organic matter of a peat layer. The field conditions relative to decomposition should on that account be carefully examined. Fluctuations in the water table, the application of lime, fertilizers and manures, methods of cultivation,—these have a very vital relation not only in the formation of surface horizons, but also to the microörganic life of the surface peat soil, and consequently upon the feeding conditions of future crops.

Oxidation produces a very noticeable change in the color of peat materials, and this coloration is one of the most obvious signs of initial decomposition. Peat layers which are submerged in water are usually of lighter color owing to the withdrawal of oxygen from the organic material.

The products of decomposition are commonly referred to as humus. Some of the products are a very dark colored, more or less resistant carbonized, earthy mixture of organic material, the characteristics of which can no longer be recognized microscopically, or based on those of the former parent layer of

peat. Other humus products are soluble; they may be taken into solution by water and used by growing plants, and they may become deposited underground or at the margin of a peat deposit. The organic material of hardpans is thus deposited as cementing material in the pore spaces of sand or silt, which they traverse. Fissures, joints, and crevices in dry peat layers frequently are filled by dissolved organic material which is precipitated from solution. A considerable part of the "doppleritic" veins and the filling of cracks and fissures in peat layers with crystals of mineral salts, deposited from solutions by water, is formed in this manner.

Humified layers of peat may be stained or their color may be changed by infiltration of suspended or dissolved organic matter, and by compounds of iron, sulfur, lime or other mineral salts. Horizons that contain considerable amounts of calcium sulfate crystals, oxidized iron, or an admixture of mineral matter washed in from uplands become proportionally more earthy upon the decomposition and loss of the organic matter. In humid regions in which the action of weathering consists of a progressive leaching of soluble material from the decomposing surface layer of peat and no carbonate is being accumulated, the humus may become distinctly acid and remain raw, resistant organic debris. Sandy subsoils develop a strongly marked gray layer, followed by a brown or yellow iron-stained horizin. In less humid areas, which differ widely in both climate and weathering, the surface layer may show horizons of humus, followed by muck over layers of peat. There is near the surface, in a definite position in the profile, an increasing accumulation of lime and other salts from ground waters, regardless of the amount existing in the original peat material or in the mineral soils below and adjoining the deposit. Leaching processes become more marked again in peat deposits of the southern coastal states where the rainfall is greater. Since humus as well as muck are a feature which has been acquired after an accumulation of peat was drained, the quantity of humus has no reference to the relative age of a peat deposit.

III. EXAMINATION OF PEAT DEPOSITS

In the conduct of a profile examination of peat deposits it is important to supply fieldmen, unfamiliar in the nature of peat investigations, with some from of field sheet for recording observations, and with published maps of the area. Time and energy can thus be conserved and the efficiency increased without loss to accuracy of detail or freedom of investigation. The form of field sheet which has been used by the writer more recently is shown in table 2. Where topographic sheets or soil maps do not exist, the fieldmen have the additional task of constructing one. This can be done, however, in the manner detailed for other surveys.

For the proper understanding of the agencies through which the several layers of peat have accumulated, careful attention is necessary to the general

TABLE 2

UNITED STATES DEPARTMENT OF AGRICULTURE

PEAT INVESTIGATION RECORD

Tally Sheet No............State..............County............................

Location of peat deposit: Twp............R..................Sect................

Name and address of owner...

..............................Name of peat deposit............................

Location of profile section: Line........Sta............Field No......Lab. No.......

....

By................................For......................Date..............

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1. *Topography*...

............................Elevation............

Acreage: Total..................% Used............

% Primitive...................% Forested..........

Depth: Max....................Min................

2. *Vegetation:* Native...................................

Dominants....................Density.............

..........................Associates...........

4. *Drainage conditions*.................................

Water Table.............inches above   surface

below

Color of water......................................

Salt content..

Sources of water supply.............................

Depth of ditches or tiles............................

Distance apart......................................

5. *Mineral Subsoil*.....................................

Character.....................Color...............

Injurious substances................................

Soils adjacent to deposit...........................

Geology of area.....................................

6. *Climatic Conditions*................................

Date of drought.................Frost...............

Unusual weather.....................................

Length of growing season............................

7. *Crop Record with best yields*.......................

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Crops of poor yield.................................

Weeds...

Plant Diseases......................................

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8. *Industrial use of peat deposit*......................

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9. *Prehistoric relics*.................................

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10. *Remarks*...

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3. *Description of profile section*, (Character, color, texture, structure of peat layer; water level, mineral subsoil).

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physiographic features of the area to be examined. Information as to whether the area represents the general features of a river valley, a terrace, an ancient glacial lake bed, an outwash plain, or a pocket in a morainal belt has a suggestive value of no small importance. A knowledge of the geology and soils of the region, the character of crops and of the native vegetation, and the nature of the water supply should be obtained beforehand to prevent errors.

The chief reason for the study and mapping of peat deposits is the occurrence, in the profile, of layers of peat tangible and definite enough so that these can be located and identified in the field. The examination consists essentially of plotting on a section map the location, distance and direction of profile soundings. To measure distances a simple odometer is generally preferred, while direction may be determined by means of a compass or a regulation sketching case.

The location of the more important profile soundings in a foot traverse should be indicated on the base map by a square mark; that of testholes by a round mark. Soundings for a detailed profile should be located by the fieldmen with reference to roads, bridges, houses, section lines or natural features shown upon the base map. Judgment must be exercised as to the number and the distance between the intermediate testborings necessary in any given area to establish changes in the character of the profile or the mineral subsoil. The necessity for detailed soundings depends upon the relative complexity of the peatland area. In a locality of obviously uniform topographic history profile soundings may be widely scattered. A change in the native vegetation or topography may indicate to the experienced field men the places and conditions which should be tested or verified by a profile. Points thus established should be sketched at once in the field as the examination progresses. For each day a tracing of the sectional peat map should be made complete in every detail with profile, legends, symbols, lettering and scale. It should be attached to the form sheet with notes, photographs or other records taken at the respective time. This procedure will aid in verifying any disagreements as to peat materials, or relating to other matters encountered in the field traverse.

In the work of identifying the botanical composition and physical character of the different layers in the profile of a peat deposit, it is necessary to examine the area from the surface downward through the entire vertical section. As a rule these examinations can be made with a peat sampler of the type illustrated in plate 5, figures 2 and 3. This instrument is a brass tube, provided with a brass plunger and with extra couplings of steel rods each two feet long, so that it can be extended to any desired depth. Augers and similar instruments of the type of a boring tool are unworkable in most peat deposits, and they introduce the serious difficulty of inaccurate measurements owing to the tearing of the fibrous or woody sample which is obtained with them.

To ascertain the variations in the profile, and the character of the different horizons and layers of peat and the mineral subsoil, it is necessary to sound

one foot at the time.   Otherwise important changes at definite depths may be overlooked.   Marked variations in color, texture, structure and degree of disintegration, the occurrence of fungi in their vegetative form, the presence of hard pan, thin seams of marl, silt, clay or of peat material charred by previous fires, should be examined and noted with some detail.   In some cases the contact or separation layer between peat and mineral subsoil is clearly marked.   In other cases, however, the texture of the peat in the presence of a considerable amount of inorganic matter makes a distinction between the two difficult to see.

The examination by means of soundings should include also the position of water pockets in or between layers of peat.   The presence of sulfuretted hydrogen is usually indicated by the odor of the peat sample and the discoloration of the brass portion of the sampling instrument.   According to recent information hydrogen sulfide is undesirable in peat deposits as it corrodes drainage pipes.   In such instances attention should be given to any marked physical differences in the peat materials, and in the mottling or chemical and mineralogical features of the inorganic subsoil.   The occurrence of highly ferruginous material, either distributed throughout the profile or in the form of concretions, near the margin of the peat deposit, or on its surface, should also be noted.   The presence of unusual amounts of vivianite, crystals of gypsum, iron pyrite, or the occurrence of incrustations in ditches and on surface soils, and any excess of soluble salts in the supply of ground-water should be examined and confirmed by laboratory methods whenever possible.   Marked acid or alkaline conditions may be tested by means of standardized litmus papers, or other indicators.

It is advisable also to inspect open drains or to dig a few holes in the ground. It is easier to obtain with a spade or large knife a smooth, vertically-cut surface, which can be observed without disturbing the layers of peat.   It will generally be observed that in some localities the color, texture, and stratification may change often fairly abruptly.   There is a further advantage from observing open ditches or digging a hole, in that the experienced fieldman can see the nature of the effects of drainage or of the mineral subsoil upon the surface horizons in the profile.   Moreover, the actual appearance of the undisturbed layers of peat may often reveal quite as much regarding the suitability of the area for certain crops or other uses, as a subsequent more laborious method of laboratory analyses.

The recognition of peat profiles and the description and identification of layers of peat on the basis of their character and arrangement constitutes, no doubt, the most important contribution that can be made by a stratigraphic study of peatland.   Great care should, therefore, be exercised in the identification and collection of peat samples in order that they may be representative of their respective area and actually represent the layers and different types of peat.   A peat material to be correlated with a type should conform in certain general features to the descriptions of peat materials referred to

before (3). The illustrations of peat materials in natural size (plates 1–5), are presented for purposes of aiding those who desire information on the general appearance of some of the usual types of peat material encountered in profiles. Variations or phases will occur at different depths or in different localities but such differences do not greatly affect their grouping. New or doubtful kinds of peat should be placed into one of the respective general, main groups of woody, fibrous, or pulpy peat, and receive a name accordingly.

The texture and structure of a peat layer are determined partly by the different admixtures and proportions of different sizes of plant remains, in part by the arrangement of the components. Some peat materials obtained in soundings from below the surface may appear unaltered and perfectly fresh; but they soon darken in color and break down rapidly on exposure to air. Occasionally an apparently unaltered peat material will begin to go to pieces after exposure for a few days or longer. Field description and structural evidence on that account are more decisive than that obtained in the laboratory. Observations in the field should not be limited to specific samples but cover a large range of variations. In this manner gradations may be traced from obscure to identifiable forms and thereby the changes peculiar to the given locality may be recognized. Alterations in dry peat samples are often extensive and varied and hence may become unsafe guides unless the local variations are known from field observations. Under conditions of over drainage very finely divided plastic colloidal peat hardens and breaks into angular fragments, in contrast to the fine textured granular product from disintegrating fibrous and woody peat layers.

In the selection of samples of peat for laboratory examination at least one representative sample for every layer or type of peat recognized in the area should be secured. If a mixture of surface material is desired small samples should be obtained from twelve to sixteen different places at some distance apart but all from the same area and layer of peat. Samples from subsurface layers and from mineral subsoils should be secured in six to ten testborings, without mixing or contamination in any way. Each of this series of samples should be packed separately into a cloth bag, glass bottle or paraffined paper box for shipment to the laboratory.

Variations in peat materials comprising a considerable range in character, texture, or structure should be recorded in the note book, and so described that they may be included in the final report. Where a good vertical section can be obtained from ditches or dug holes it will be advisable to separate the profile into a series of brick shaped sections, and to label and pack each separately. The location of samples and other material collected in the progress of the examination, should be carefully noted in the field book. The profile soundings from which samples are taken and submitted for further study should be indicated on the base map with a serial number.

For possible extensive laboratory or greenhouse work samples from various depths or localities should be taken in adequate amounts; they should be

collected during the progress of the field work, rather than at the completion
of the survey. It is frequently impossible to collect at a later period on ac-
count of unfavorable weather conditions or lack of time.

The tags attached to field samples of peat should have the field serial num-
ber and should indicate the location of the place from which the material
was obtained, its depth, the date, name of the collector, and remarks if neces-
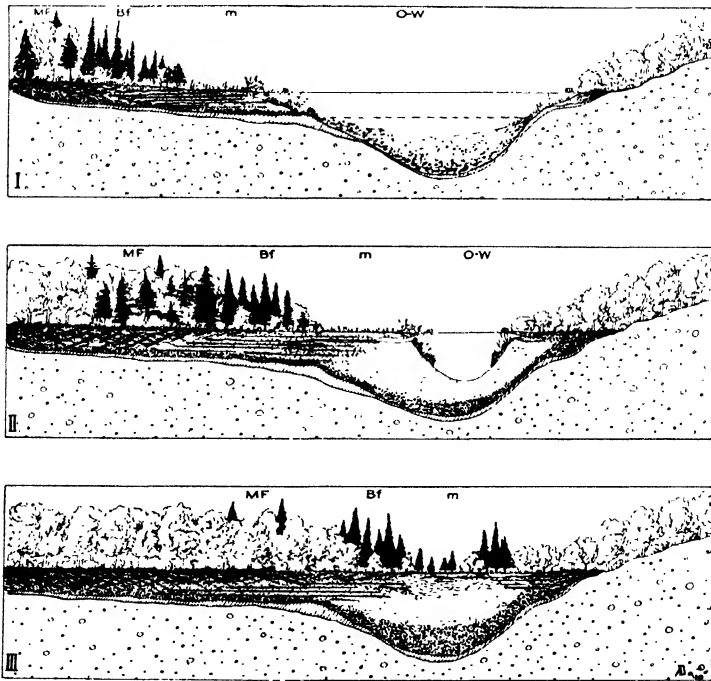
FIG. 1. GRAPHIC PRESENTATION OF THE DEVELOPMENT OF A PEAT DEPOSIT

The diagrammatic profile illustrates also the character, location, and continuity of dif-
ferent layers of peat.

sary, concerning the examination desired. This information should be written
in ink or indelible pencil, and it should be in general accord with the more
detailed description given in the field sheet.

After the observed facts relative to the several profile soundings are as-
sembled certain inferences can be made as to the surface conditions in peat
areas lying between points of actual observation. Similar inferences can
also be drawn as to the conditions beneath the surface and expressed in
vertical diagrams; the cross sections should represent the profile that would
be exposed by making a vertical cut down through the entire peat deposit

FIG. 2. GENERALIZED CROSS-SECTIONS TO SHOW SERIES OF THE MORE COMMON TYPE
PROFILES IN THE TWO GROUPS OF WATER-LAID AND LAND-LAID PEAT DEPOSITS

along certain selected lines (fig. 1). Diagrams of profile sections are a great aid to a thorough comprehension of the conditions of a peat deposit along a line of traverse; they visualize the space and time relations represented by a peat area. Differences in peat layers and peat profiles should be shown graphically by the use of certain symbol-patterns inserted in the text. In figu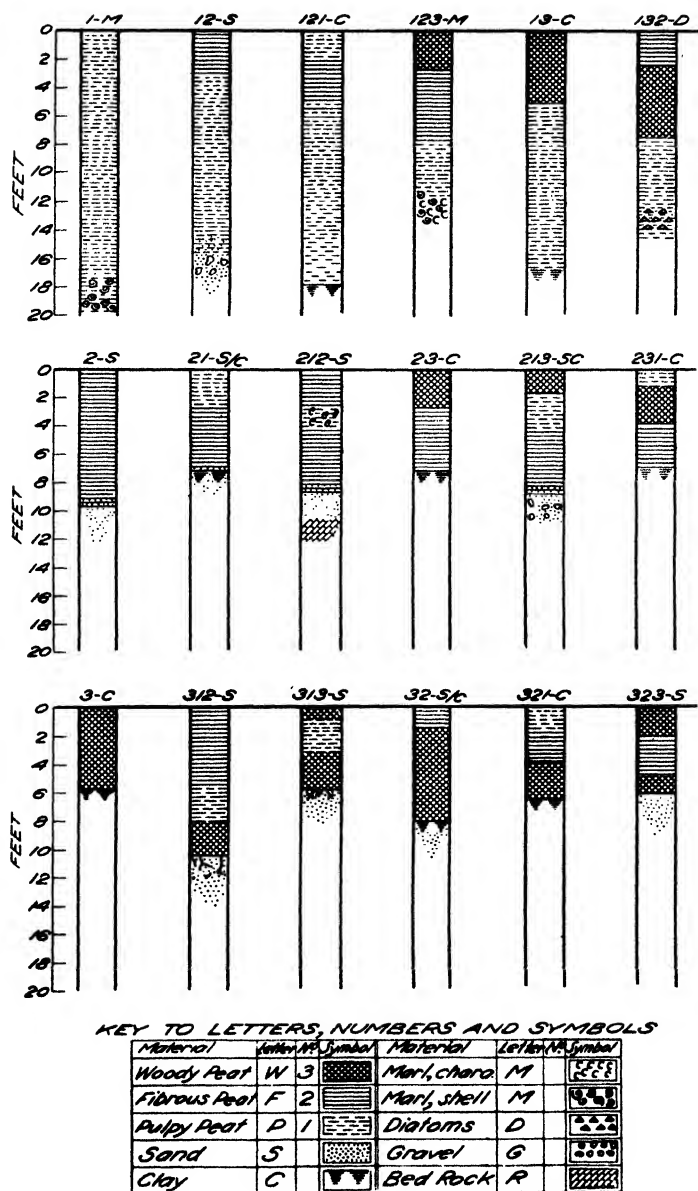re 2 are shown the conventional letters and symbols employed to represent respectively the character and thickness of the several peat layers, and the nature of the mineral subsoil in the profile. Horizons and layers which are not sharply defined in the profile of a deposit are indicated by a merging of boundary lines.

A peat map is a graphic illustration of all available information assembled in proper relations, pertaining to the surface and the stratigraphic features of peat deposits in a given locality. A peat map should show, therefore, not only the boundary lines between different type profiles in so far as is clearly warranted by observed facts, but also the whole thickness of each deposit. The following colors to represent differences in depth of peat accumulation are suggested: a light brown color for shallow peat deposits varying from eight inches up to three feet in depth; a dark brown color for peat areas of greater depth than three feet. Differences in type profiles and their characteristics should be indicated by means of numbers or some other conventional designation. Cartography and graphic methods have made considerable advance in foreign countries, notably the Scandinavian countries, Russia, and Germany.

In figure 2 is shown a series of the more common type profiles in each group of peat deposits encountered in field work. The numbers used to express these units of mapping are combinations based on the group number of the respective peat layers in the profile, beginning at the bottom of the section. In these numbers the first and last numeral deserve special attention: the former implies the original position of the water table, and hence the extent to which the peat area can be drained; while the latter numeral denotes the surface peat layer which is or will be influenced by soil forming processes. A great many sub-types may be recognized upon the basis of differences in thickness, texture and structure of layers, and in surface horizons of disintegrating organic material in drained peat areas, but all have the generalized profiles as stated. Profile numbers may be shown on the completed map as overprints together with the symbol pattern indicating the nature of the mineral subsoil.

The writer believes that the field methods here outlined will make it possible not only to determine the actual extent and location of peatland resources, but also to take up relationships to the practical utilization of selected peat areas for crops, pasture, reforestation, wild life reserves or other purposes. The method is offered as an aid toward furthering peat investigations, farming practices and state and national peatland policies.

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PLATE 1

FIG. 1. Brown, compact, plastic, coarsely divided, pulpy peat of sedimentary origin. Natural size.

FIG. 2. Finely divided colloidal peat which hardened and cracked upon drying; it possesses conchoidal fracture and breaks into angular fragments. Natural size.

FIG. 3. Brown, coarsely divided, pulpy peat with an admixture of fibrous plant remains from reeds. Natural size.

FIG. 4. Surface view of black, friable, pulpy peat with shells. Natural size.

FIG. 5. Gray brown pulpy peat with portions of reed plants infiltrated with iron—Surface view. Natural size.

FIG. 6. Surface view of brown Hypnum peat. Natural size.

FIG. 7. Black, friable, sedimentary peat with marl from shells—Side view. Natural size.

FIG. 8. Dark brown, sedimentary peat containing nodular concretions of iron—Side view. Natural size.

FIG. 9. Brown finely fibered Hypnum peat on gray silt—Side view, showing well-marked line of separation between organic material and mineral subsoil. Natural size.

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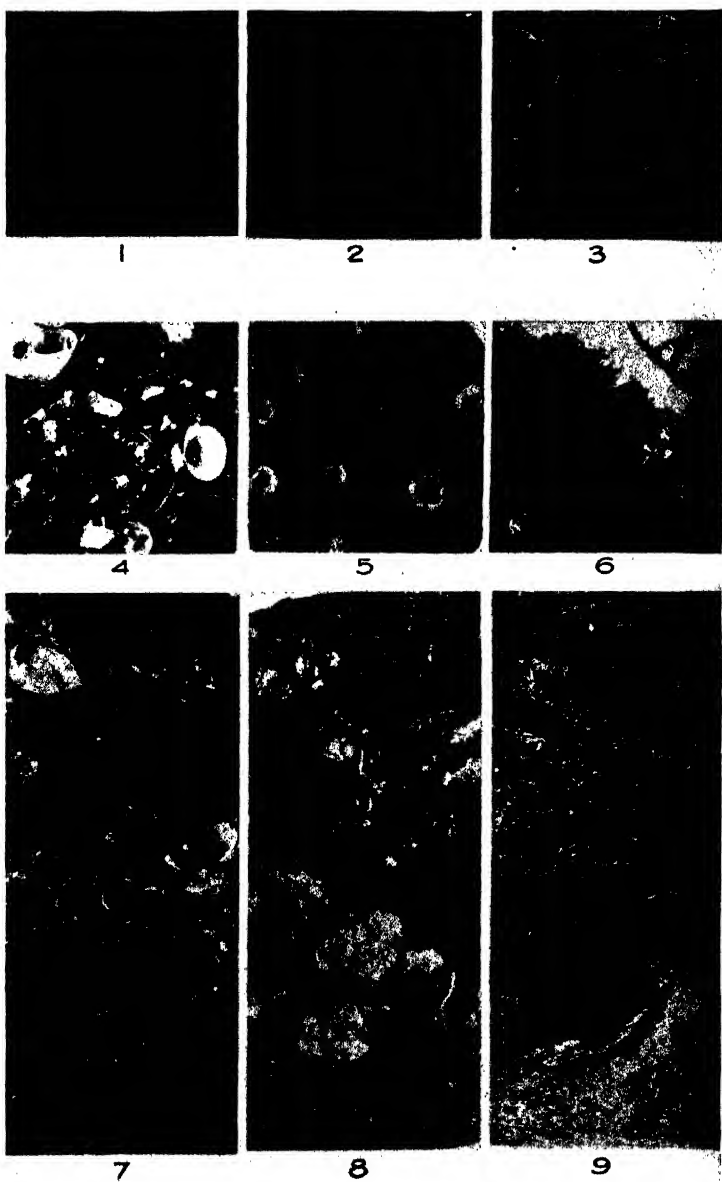
PLATE 1

PLATE 2

Fig. 1. Light brown, coarse, fibrous reed peat. Natural size.
Fig. 2. Dark brown, finely-fibered, felty sedge peat. Natural size.
Fig. 3. Brown, porous, matted coarsely-fibered reed peat. Natural size.

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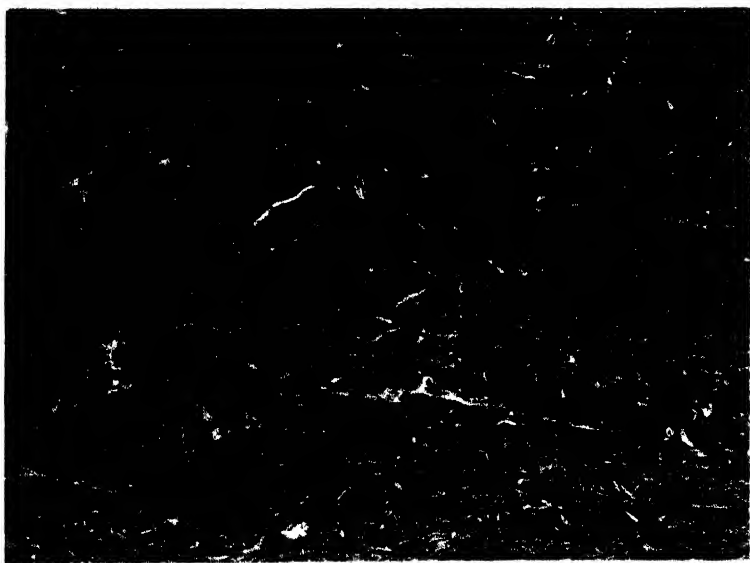
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PLATE 3

FIG. 1. Brown, loose, coarsely fibered sedge peat—Cross section of a layer floating as a mat near the margin of a pond. Natural size.

FIG. 2. Gray-brown, loose coarsely fibered sphagnum peat—Side view of a section cut from a surface layer. Natural size.
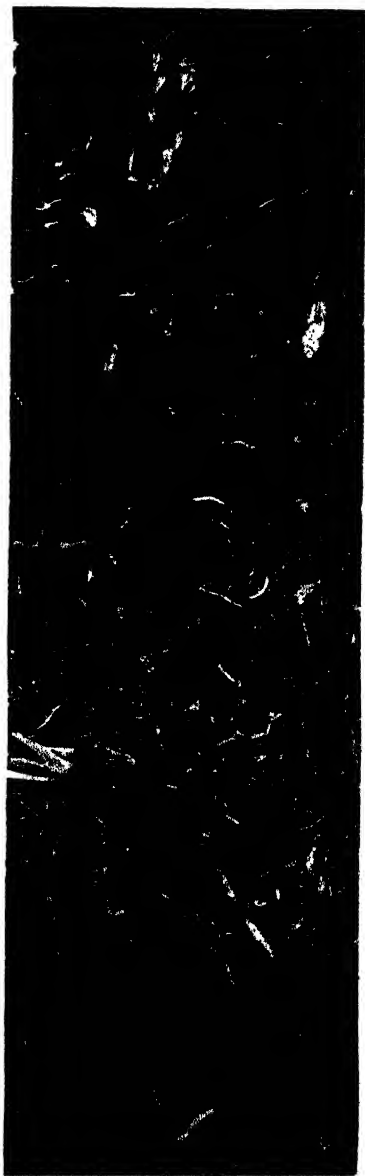
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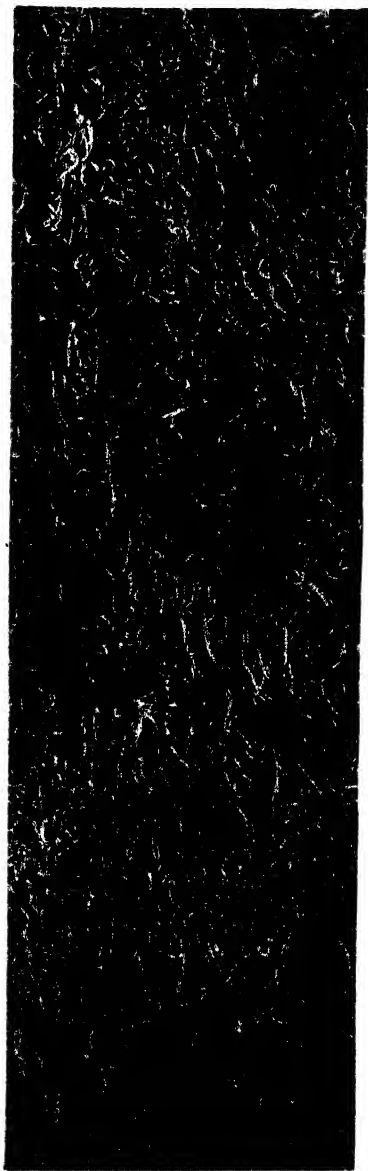
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PLATE 4

Gray-brown fibrous sphagnum peat resting on a layer of finely-fibered, dark brown, compact sedge peat; the woody material in the horizons at *a* and *b* is derived from heath shrubs growing as a surface vegetation—Side view of a cross section cut from the surface. Natural size.

a

b
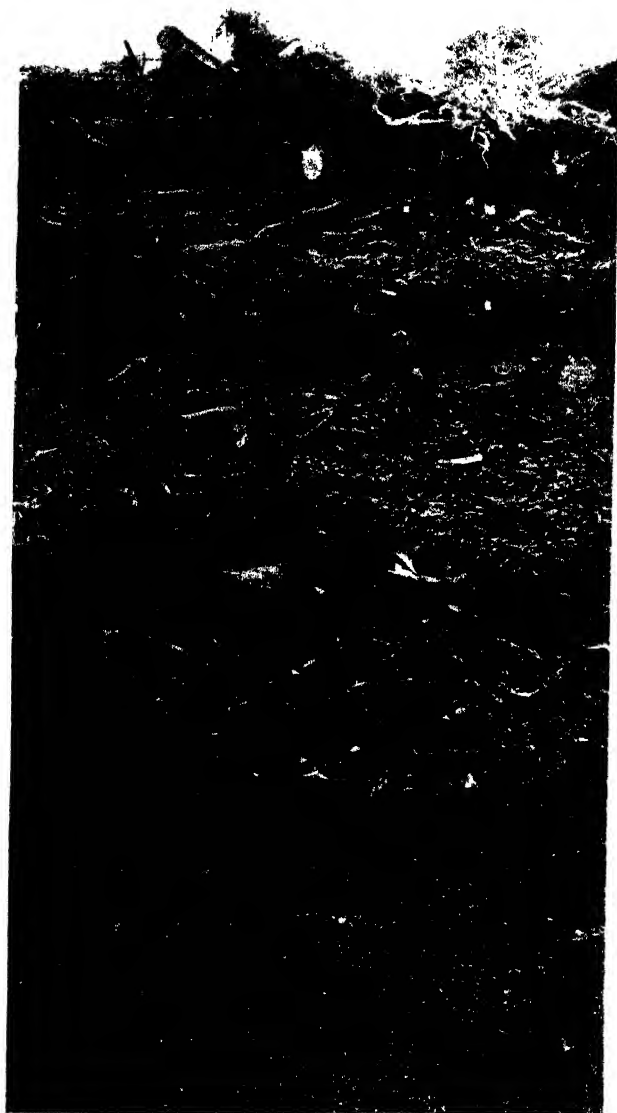
Fig. 1. Dark brown, loose, forest peat containing varying amounts of coarsely fragmented woody material, root fibers, and well disintegrated granular debris—Side view of a cross section cut from the surface layer. Natural size.

Fig. 2. Brass instrument used for profile soundings of peat deposits. One-half natural size.

Fig. 3. Brass plunger, withdrawn from the brass cylinder to show spring with catch which locks the instrument at any desired depth. The cylinder, when filled with peat, protects the sample from any contamination with other material.

EFFECT OF IGNITION AT VARIOUS TEMPERATURES UPON CERTAIN PHYSICAL PROPERTIES OF SOILS

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INTRODUCTION

It is generally known that igniting mineral soils to very high temperatures produces very marked change in their physical condition which in turn affects greatly their physical properties such as texture, structure, plasticity, absorption, water-holding capacity, etc. This change is particularly noticeable in the colloidal types of soil. Very little, however, is known regarding the degree of change of these properties at various temperatures of ignition, and especially the particular temperature at which the change commences to take place.

In connection with studies on soil temperatures that are being conducted by this laboratory it appeared very desirable and important to make a study of the degree of change brought about in soils by igniting them at different degrees of temperature. As a measure of this change three distinctly different properties were chosen for comparative study; viz., heat of wetting, unfree water and plasticity. These three properties were studied for each soil at several degrees of ignition from quite low to very high. It was thought originally that the results obtained from these studies would not only be of interest in showing the initial temperature at which the change commences and the degree of change that takes place at the various temperatures of ignition but also that they might probably suggest or furnish the much needed method of estimating the colloidal content of soils.

METHOD AND PROCEDURE

For igniting the soils an electric furnace was employed. The temperature of this furnace was measured by means of a couple which was standardized and was accurate to within 10°C. Four different degrees of temperature were finally adopted for igniting the soils. These are 110°, 230°, 485°, and 800°C. The furnace was kept regulated so that these temperatures remained quite constant. The soils were heated at these various temperatures for a period of about seven hours. After they had cooled, their heat of wetting, unfree water and plasticity were studied. The heat of wetting was measured according to the method described in former publication (1). It consisted of placing 50 gm. of air-dry soil in a wide glass tube and allowing it to dry in an electrically heated oven at a temperature of 110°C. for 24 hours. The tube was taken out, closed with a rubber stopper and allowed to attain the room temperature. After the exact weight and temperature were ascertained, the soil was quickly

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and carefully poured into a calorimeter containing 100 grams of water, and the heat of wetting was ascertained.   Extreme care was taken before mixing to have both the soil and water at exactly the same temperature and very nearly that of the room temperature.   In order to be able to convert, if necessary, the rise of temperature into heat calories, the water equivalent of the calorimeter was determined.   This was found to be 25 gm.   For the specific heat of soils, the value of 0.200 was employed for the mineral soils and 0.300 for the organic soils unburned.   For the burned organic soils, the same value was used as in the case of the mineral soils.

The unfree water was measured by means of the dilatometer method, already described (1).   The moisture content employed was at the proportion of 20 gm. of soil to 15 cc. of water.   Before the final measurement was made the soils were subjected to freezing and thawing once or twice.   The soils were then placed at a temperature of 1.5°C. and allowed to come to equilibrium and the volume on the dilatometer stem recorded.   They were then immersed at a temperature of about 12°C. for about fifteen minutes, and then returned to the original temperature.   After equilibrium was attained the volume on the dilatometer stem was again read and from the two readings the unfree water could be calculated.   The term unfree water is used in this paper to designate the soil water remaining unfrozen at the temperature of slightly below zero.   All the water which freezes very readily or at very near zero is designated as free water.   The free water is beyond the direct influences of the soil and consequently is not at liberty to freeze as the free water.

In the case of the plasticity measurements, unfortunately there is no scientific method and recourse had to be made to the old finger-test.   Although no accurate measurements can be made by such a method, by practice one can learn to estimate and compare the plasticity of the soils fairly well, and it is believed that in the present study, a measurable change in the plasticity of soils as influenced by the various degrees of ignition could be detected.

<div align="center">EXPERIMENTAL</div>

In table 1 are presented the results on heat of wetting and in table 2 the data on unfree water.

Examining first table 1 some very interesting facts are revealed.   In the first place it is at once seen that the igniting of soils tends to decrease the property of heat of wetting.   But this decrease does not become appreciable until rather high temperatures of ignition are reached.   At the temperature of 230°C.$_2$ for instance, the decrease amounts to only about 5 per cent for many soils, taking the temperature of 110°C. as a standard which is generally used for drying soils.   In some soils the decrease amounts to more than 5 per cent but this is true mainly in soils which contain considerable amount of organic matter, such as the Iowa Carrington clay loams.   On the other hand some other soils such as the Minnesota black surf which also is rich in organic matter does not show very much change and in the case of the peats and mucks there is an actual increase instead of a decrease in the heat of wetting.   This increase is apparent even at the ignition temperature of 485°C.   These results of the peats and mucks are contrary to those of the mineral soils and the possible explanation for them may be that many of the organic particles are resistant to wetting and also they are so hard that water penetrates into them with exceedingly slow rate and great difficulty.   The higher temperatures probably helps to destroy that resistance to wetting and also cracks the hard particles, with the result that more surface is wetted at the

higher temperatures of heating than at the low and consequently more heat is given off.

The intermediate temperature of 170°C. was also tried but the results obtained showed that in many of the soils the heat of wetting was practically the same as that at 110°C. Hence this intermediate temperature was abandoned in favor of that at 230°C., which may be considered as the temperature at which a measurable change in physical condition of the soil commences to take place.

TABLE 1

Effect of ignition on the heat of wetting of soils

Rise of temperature caused by 50 gm. of soil in 125 gm. of water

SOILS	HEAT OF WETTING			
	Ignited at 110°C.	Ignited at 230°C.	Ignited at 485°C.	Ignited at 800°C.
	°C.	°C.	°C.	°C.
Penn silt loam................................	0.90	0.80	0.50	0.0
Ohio silt loam................................	0.80	0.70	0.35	0.0
Michigan clay loam...........................	2.10	2.00	1.85	0.0
Iowa Carrington clay loam....................	3.40	2.85	1.20	0.0
Minnesota black surf.........................	2.85	2.70	0.65	0.0
Illinois clay loam............................	3.50	2.95	1.45	0.0
Michigan clay................................	1.65	1.40	0.75	0.0
Illinois red clay..............................	3.50	3.20	1.60	0.0
Wisconsin Superior clay.......................	1.95	1.40	0.95	0.0
California Merced clay........................	4.00	3.80	1.70	0.0
Upper Michigan clay..........................	2.05	1.90	1.00	0.0
Muck..	8.6	11.50	10.00	0.0
Peat...	10.50	13.00	11.50	0.0
Fullers earth.................................	8.00			0.0
Ferric hydroxide.............................	3.75			0.0
Silica gell...................................	9.60			0.0
Aluminum hydroxide.........................	8.35			2.4

The data in table 1 further showed that at the ignition temperature of 485°C. the heat of wetting of all the soils except the peat and muck, has been considerably reduced, but it is still quite appreciable, in most of the soils, the decrease being less than 60 per cent of the original. This comparatively small decrease is very significant in showing that the physical constitution and properties of the soils which give rise to the heat of wetting are very resistant and are not destroyed or radically altered even at as high temperature as 485°C.

On the other hand the same table shows that as soon as the ignition temperature of 800°C. is reached, the properties of the soil which give rise to the heat of wetting are totally and completely destroyed and the property of heat of wetting completely disappears. This is true of all the soils, both inorganic and organic, the only exception being that of aluminum hydroxide

which still gives heat of wetting at the highest temperature due probably to hydration. Outside of the last material, all the soils and other artificial materials failed to give any heat of wetting whatever when they were ignited at the temperature of 800°C.

These results are not only interesting *per se* but they are also very significant in suggesting the possibility that a method might be evolved for estimating the colloidal condition or content of soils and the degree of activation. There is no doubt, of course, that the material which gives rise to the phenomena of heat of wetting is the colloids of the soil and their degree of activation. Since this phenomenon of heat of wetting completely disappears upon ignition at a certain temperature it logically follows that the colloidal content or state is completely destroyed by the heat at that temperature. That such is the

TABLE 2

Effect of ignition on unfree water in soils

SOILS	UNFREE WATER IN SOILS			
	Ignited at 110°C.	Ignited at 230°C.	Ignited at 485°C.	Ignited ot 800°C.
	per cent	*per cent*	*per cent*	*per cent*
Penn silt loam................................	7.5	7.0	6.5	0.0
Ohio silt loam................................	3.5	3.3	2.8	0.0
Michigan clay loam...........................	13.6	12.0	9.5	0.1
Iowa Carrington clay loam....................	16.5	13.7	12.0	0.0
Minnesota black surf.........................	14.0		2.75	0.0
Illinois clay loam............................	16.0	15.5	10.5	0.6
Michigan clay................................	10.2	11.0	8.5	0.0
Illinois red clay..............................	17.2	18.0	16.0	3.0
Wisconsin Superior clay......................	16.5	13.7	10.8	2.7
California Merced clay.......................	21.2	19.8	16.2	2.0
Upper Michigan clay.........................	16.4	15.0	14.0	2.1

case appears to be proved by the fact that upon grinding the burned soils including the most colloidal clays, to as fine condition as it is possible to grind them and then determining again their heat of wetting, it is found that they lack this property just as before grinding. That this property of soils can be completely destroyed by ignition irrespective of the resulting fineness of particles is further shown by the data on ashes of mucks and peats. The ashes of these materials of course are extremely fine and yet they give no heat of wetting. These results are important and significant.

From these general data on the effect of ignition on the heat of wetting, a method appears to be suggested for estimating the colloidal state or content of soils and their degree of activation. This problem is now under extensive investigation.

Considering next table 2 it is also seen that ignition tends to decrease the unfree water in soils. The amount of unfree water is greatest in the unburned

soils, then becomes smaller with the increased temperature of ignition and becomes exceedingly small or entirely disappears when the soil has been heated at 800°C. These results correspond and agree with those on the heat of wetting.

The effect of ignition on plasticity was studied on several heavy clays including Michigan clay, California Merced clay, California Stockton clay, Illinois clay loam, Illinois red clay, Nebraska Pierre clay and Decatur clay. The results obtained show that when these soils were heated at 230°C. the plasticity in all cases was, as far as could be ascertained, the same as before heating. Heating them to 485°C. the plasticity, in all cases, disappeared almost completely in the original structure, but was greatly restored by grinding them. Heating them to 800°C. the plasticity in all of these disappeared completely both before and after grinding.

These results, therefore, agree with those on heat of wetting and unfree water, and they all go to show that these three properties are affected by heating in the same way, i.e., they begin to be affected at the same initial temperature and they are completely destroyed at the same degree of temperature.

SUMMARY

An investigation was conducted to study the effect of heating of soils at various temperatures upon the degree of change that takes place in the soils and the temperature at which the change commences, and ends. Three physical properties of the soils were chosen upon which to study this change, namely, heat of wetting, unfree water and plasticity.

It was found that all these three properties begin to be affected at about the same initial temperature which is about 230°C. At this temperature a change in these properties just commences to be perceptible.

At the temperature of 485° all three properties are greatly reduced, but they are not as yet entirely destroyed. At the temperature of 800°C., however, they become entirely destroyed and completely disappear.

When soils are heated to 800°C. no matter how fine they are ground again they give no heat of wetting. Even ashes of peats and mucks give no heat of wetting, even though they are so exceedingly fine. These results strongly suggest the possibility of evolving a method of determining or estimating the colloidal content or condition of soils, and their degree of activation.

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MICROBIOLOGICAL ANALYSIS OF SOIL AS AN INDEX OF SOIL FERTILITY: VII. CARBON DIOXIDE EVOLUTION[1]

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HISTORICAL

The evolution of carbon dioxide has been used by a number of investigators as an index of the decomposition of organic matter in the soil.

Wollny (38) found in 1880 that the carbon dioxide content of the soil rises and falls with the amount of organic matter present in the soil. Kiszling and Fleischer (8) used the production of carbon dioxide in peat soils as an index of the rapidity of the decomposition going on in the soil; the addition of sand was found to stimulate oxidation, while the temperature was among the most important factors affecting oxidation.

Déhérain and Démoussy (2) placed the soil under examination in a closed tube of 100 cc. capacity and kept it at constant temperature. At the end of a certain period of incubation, the gas was extracted and the carbon dioxide present determined. It was found that the formation of carbon dioxide was due almost entirely to the action of microörganisms and that the carbon dioxide content increased with temperature to about 65°C., then decreased, and at 90° another increase took place due to chemical agencies. There is an optimum moisture content for the formation of carbon dioxide, which is also influenced by the state of division of the soil and its aeration. Although sterile soils were found to produce small amounts of carbon dioxide, the latter increased twenty-five times when soil infusion was added [Severin (23)]. Sterilized and inoculated soil gave two to five times as much carbon dioxide as unsterilized and uninoculated soil.

Russell (21) measured the actual amount of oxygen absorbed by the soil as an index of soil oxidation instead of determining the carbon dioxide produced. He found that the rate of absorption of oxygen increased with temperature, the amount of water (up to a certain point) and the amount of calcium carbonate present in the soil. These conditions also increase soil fertility. Russell, therefore, suggested the use of soil oxidation as a measure of fertility. The amount of oxygen absorbed measures the total action of soil microörganisms, which are responsible for the decomposition processes in the soil.

Stoklasa and Ernest (30) placed 1-kgm. portions of sieved soil in glass cylinders through which a current of air was passed at the rate of ten liters in twenty-four hours. They observed that the evolution of carbon dioxide by a soil, under certain conditions of moisture and temperature, in a certain length of time, can furnish a reliable and accurate method for the determination of bacterial activities in the soil; the presence of organic matter and the temperature were found to be of greatest importance. Stoklasa (25, 26) further found that the evolution of carbon dioxide occurs most abundantly in neutral or slightly alkaline soils, abundantly supplied with readily assimilable plant nutrients and well aerated.

The production of carbon dioxide [Stoklasa (27)] was in direct proportion, not to the total carbon content of the soil, but to the available organic matter in the soil. The evolution of

carbon dioxide was thus found to be an index of the availability of the soil organic matter, or the ease with which it decomposes. Two methods were suggested by Stoklasa (27, 28, 29) to demonstrate this; (1) the determination of the amount of carbon dioxide produced in twenty-four hours by 1 kgm. of soil remoistened after first being air-dried and (2) sterilizing the soil and then inoculating 1 kgm. with 10 gm. of cattle manure extract and determining the amount of carbon dioxide produced in twenty-four hours. The two methods gave the following results:

SOIL TYPE	CARBON CONTENT	CO_2 PRODUCED IN 24 HOURS BY 1 KGM. OF FRESH SOIL	CO_2 PRODUCED IN 24 HOURS BY 1 KGM. OF STERILIZED, INOCULATED SOIL
	per cent	*mgm.*	*mgm.*
Tenacious clay soil..........................	1.68	8.2	14.0
Diluvial loam.............................	2.12	14.6	27.8
Alluvial soil..............................	1.73	36.6	59.8

The amount of carbon dioxide produced was found to depend on the quantity and kind of organic matter, physical and chemical condition of the soil, numbers and kinds of microörganisms. It was found to serve as an index not only of the activities of the microörganisms of the soil but of the amount of readily decomposable organic matter.

Carbon dioxide evolution was thus found to run parallel with numbers of microörganisms and also [Stoklasa (27)] with nitrification in the soil, as shown in the following table:

SOIL DEPTH	UNCULTIVATED, UNFERTILIZED LOAM SOIL		CULTIVATED, FERTILIZED, UNDER CLOVER		MANURED AND FERTILIZED, CULTIVATED UNDER BEETS	
	Bacteria in 1 gm.	CO_2 by 1 kgm. in 24 hours	Bacteria in 1 gm.	CO_2 by 1 kgm. in 24 hours	Bacteria in 1 gm.	CO_2 by 1 kgm. in 24 hours
cm.	*thousands*	*mgm.*	*thousands*	*mgm.*	*thousands*	*mgm*
10–20	230	16.5	· 1,800	38.6	4,700	47.5
20–30	256	19.4	2,350	38.8	3,529	49.7
30–50	208	9.8	1,600	20.2	2,100	28.5
50–80	14	3.3	540	6.3	184	6.6
80–100	5	2.1	72	2.7	95	2.3

Van Suchtelen (32) passed a current of air, usually 16 liters in 24 hours, through 6 kgm. of soil placed upon pure sand in a jar. The intensity of carbon dioxide production was found to be much greater at the beginning of the experiment and rapidly decreased after a short while. The amount of carbon dioxide produced was measured until it reached a uniformly low level; the average amounts of carbon dioxide produced per unit time from the different soils served for comparison. He concluded that the determination of carbon dioxide formation by different soils furnishes a better means for estimating the bacterial activities in the soils than the numbers of bacteria. Cultivation, aeration and nutritive salts were found to exert stimulating effects upon carbon dioxide production; moisture and organic matter content of the soil are among the most important factors. In a later contribution, van Suchtelen (33) considered the microbiological activities in the soil from the standpoint of energy. The amount of heat produced by a given soil under laboratory conditions, during a definite interval of time, was taken as a unit of comparison.

Rahn (20) used sugar solutions containing $CaCO_3$ and inoculated with soil; he measured not only the carbon dioxide produced by the microörganisms from the sugar but also that formed from the interaction of organic acids with $CaCO_3$. The use of carbon dioxide production in soil as a measure of soil fertility was also suggested by König, Hasenbäumer and Glenk (11), who measured the carbon dioxide evolved from 1 kgm of soil with and without the addition of 1 gm. of glucose or urea.

Russell and Appleyard (22) found the curves for bacterial numbers, nitrate and carbon dioxide content of the soil air sufficiently similar to justify the view that all these phenomena are related. A rise in bacterial numbers was accompanied by a rise in the carbon dioxide content in the soil air and somewhat later by a rise of nitrate in the soil. The rate of decomposition of organic matter in the soil was, therefore, looked upon as a function of bacterial activity. The rate of biochemical activities in the soil was found to attain maxima in late spring and in autumn, and minima in summer and winter. In autumn the bacteria increased first, then the carbon dioxide content rose, and finally the nitrate increased.

Most of the early work and considerable later work on carbon dioxide in soils has been carried out with the gases taken from the soils *in situ*. A large amount of such work seems to demonstrate the difficulties of obtaining indicative results by analyzing the atmosphere of field soils in place.

Pettenkofer (18) suggested a method for measuring the carbon dioxide produced by soils. He aerated soils with carbon dioxide free air through a container and measured the carbon dioxide in the outgoing air.

Petersen used a similar apparatus (17) and since then the Pettenkofer method has been used extensively by numerous investigators with various modifications. Among these might be mentioned Wollny (39) who aerated the soil mixed with sand, Déhérain and Démoussy (2) Stoklasa and Ernest (30), van Suchtelen (32), Lemmermann, et al. (13), Klein (9), and Gainey (6).

Russell (21), and Darbishire and Russell (1) used oxygen consumption, to measure soil oxidation processes. Leather (12) extracted the gases from the soil samples by suction and subsequently analyzed them for carbon dioxide.

Few of these methods have been used to any extent recently. The method commonly used at present is to measure the carbon dioxide in air, previously freed from carbon dioxide, passed continuously over the surface of soil placed in containers. Under these conditions the soil more nearly approaches normal conditions than where it is aerated, which greatly accelerates microbiological activities. This method has been used by Fred and Hart (5), Fraps (4), Potter and Snyder (19), Merkle (14), Neller (15) and has proved satisfactory in our hands.

Potter and Snyder (19) state that the amount of air passing over the soil in the laboratory does not materially affect the amount of carbon dioxide evolved. The addition of moisture to an air-dry soil was found to result in a rapid increase in the amount of carbon dioxide evolved, followed by a gradual drop. Previous drying of the soil alters its colloidal condition, permitting an increased rate of oxidation. It also alters the chemical condition of the organic matter making it more readily available for the activities of microörganisms. Similar results were obtained by Klein (9) and others.

Neller (16) determined the carbon dioxide producing capacity of the soil by placing tumblers containing 200-gm. portions of soil, to which 0.75 gm. of soybean hay had been added, under bell jars, through which carbon dioxide free air was passed for sixteen days. On comparing two limed and two unlimed soils, he obtained distinct correlations between crop yield, nitrate accumulating and numbers of bacteria, but these did not correlate with ammonia accumulation, as shown below:

PLOT NUMBER	CROP YIELD (10 YEARS)	CO_2 PRODUCTION	NO_3-N* ACCUMULATION	NH_3-N* ACCUMULATION	BACTERIAL NUMBERS
	lbs.	mgm.	mgm.	mgm.	millions
11A (acid)	2282.4	353.4	10.3	11.93	2.5
11B (limed)	2928.0	505.6	22.3	11.44	6.2
21 (acid)	2015.8	389.9	16.1	11.56	5.1
24 (limed)	2661.1	542.0	33.9	11.68	6.5

* From 100 mgm. nitrogen in the form of dried blood.

König and Hasenbäumer (10) also found that carbon dioxide formation goes hand in hand
with bacterial numbers. Gainey (6) observed the parallel formation of carbon dioxide,
ammonia and nitrate from organic substances rich in nitrogen (cottonseed meal and dried
blood), when moisture and aeration were favorable; the correlation was especially notice-
able between the ammonia and carbon dioxide production.

The discrepancy between Neller's and Gainey's results can be readily explained by a
consideration of the carbon and nitrogen metabolism of the microörganisms concerned, espe-
cially the fungi. It will be shown elsewhere that the relative amounts of carbon dioxide and
ammonia formation from any organic substance depends upon the metabolism of the particu-
lar organism and the carbon-nitrogen ratio of the organic material. For every unit of carbon
assimilated by the organism, as well as for the carbon dioxide formed, there is a definite amount
of nitrogen assimilated. When the organic matter (dried blood or cottonseed meal) contains
more nitrogen than the organism needs for metabolic processes, a part of the nitrogen will be
left as a waste product in the form of ammonia; when the organic matter contains less nitro-
gen than the organism requires, there will be no ammonia accumulation and the carbon com-
pound will be decomposed only so far as the nitrogen supply, whether present in the material
or added in inorganic forms, will permit.

Gainey determined the carbon dioxide formation and ammonia accumulation from nitro-
gen-rich organic materials, such as dried blood or cottonseed meal. It would be expected
that both would run parallel, since for every unit of carbon used up, either for structural or
energy purposes, there is a corresponding amount of nitrogen liberated, as ammonia, in excess
of that required by the organism. Neller, however, determined carbon dioxide production
from soybean meal, a substance comparatively low in nitrogen, and ammonia formation from
dried blood. The rate of decomposition of these two substances in the same soil, as indicated
by the evolution of carbon dioxide, is different, as shown by Starkey (24).

It is also important to point out that the formation of carbon dioxide in the soil depends
not only upon the absolute carbon content of the soil, but upon the ease of its decomposition,
as shown by Stoklasa (27) and Gehring (7).

A brief review of the literature, therefore, tends to indicate that the evolution of carbon
dioxide is a good index of decomposition of organic matter, of microbial activities and of soil
fertility. The fact that the numbers of microörganisms and the nitrifying capacity of soil
have been found in previous investigations (34, 36), to be good indices of soil productivity
and the fact that Stoklasa (28, 29), Russell and Appleyard (22), Neller (15), van Suchtelen
(32) and others found that evolution of carbon dioxide runs parallel to bacterial numbers and
to the nitrifying capacity of the soil, tend to emphasize further that we are dealing here with
an important soil microbiological process, which may serve as a proper index for a microbio-
logical analysis of the soil.

METHODS

In studying the power of the soil to decompose organic matter, we often
use the terms "oxidative capacity," "carbon dioxide producing capacity,"
"capacity for decomposing organic matter," "respiratory capacity of soils,"
etc., all of which mean about the same, namely the decomposition of organic
matter in the soil by microörganisms, whereby energy is liberated. Carbon
dioxide may be formed not only as a result of oxidation, but as a result of
hydrolysis, as in the case of formation of alcohol and carbon dioxide from ·
dextrose.

$$C_6H_{12}O_6 = 2C_2H_5OH + 2CO_2$$

On the other hand, energy may be liberated without the formation of carbon dioxide, as in the case of the anaerobic transformation of dextrose to lactic or acetic acids.

$$C_6H_{12}O_6 = 2CH_3CHOH \cdot COOH \ (+ \ 15 \ Cal.)$$
$$C_6H_{12}O_6 = 3CH_3 \cdot COOH \ (+34 \ Cal.)$$
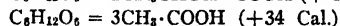
Some carbon dioxide undoubtedly also originates in normal soils from carbonates interacting with organic or mineral acids by biological agencies.

The absorption of oxygen would also be only a partial index of energy transformation, since some energy is liberated without the intervention of free oxygen. It would, therefore, be more accurate to use the calorific value of the soil, or liberation of heat as a result of the activities of microörganisms, as an index of energy transformation, as suggested by van Suchtelen (33). However, in view of the complex apparatus necessary for the determination of the latter and in view of the fact that the carbon dioxide is a final product of energy utilization by the majority of heterotrophic soil microörganisms, while only a small amount of it is reassimilated by the autotrophic bàcteria, we may use the evolution of carbon dioxide as an index of respiration of soil microörganisms without danger of introducing appreciable errors.

A differentiation should be made between the "respiratory power of the soil" itself and the "decomposing power of the soil" or its ability to decompose added organic matter. Respiratory power is measured by the carbon dioxide produced (from the soil itself), when a definite amount of soil is placed under optimum conditions of moisture and temperature. This depends upon:

1. The number and kind of microörganisms present. 2. The amount of organic matter in the soil. 3. The composition of this organic matter (the degree of its decomposition). 4. Soil aeration. 5. Moisture content. 6. Physical condition of the soil. 7. Chemical composition (altered by fertilization). 8. Soil reaction. 9. Kinds of plants grown (Stoklasa, 25).

Decomposing power is measured by the rate at which a soil decomposes organic matter added to it. It is influenced by most of the factors mentioned above, particularly by the microbial population and the physical and chemical conditions of the soil. Furthermore, a difference in the composition of the organic matter used will effect a change in the activity of the various groups of soil microörganisms and different soil constituents may become limiting factors, e.g., nitrogen or phosphorus, if the added organic matter is low in these.

The amount of carbon dioxide produced in sterilized soils inoculated with a strong cellulose-decomposing organism, preferably a rapidly growing fungus may also be measured. This is preferable to the use of manure, as done by Stoklasa, since no additional nutrients are added with a pure culture.

The "respiratory power of the soil," which indicates the condition of the organic matter in the soil, its ease of decomposition or its availability, when the soil is brought under favorable temperature and moisture conditions, as

well as activities of microörganisms in the given soil or their respiration intensity can be determined in three different ways:

1. One-kilogram portions of fresh soil, from a composite sample taken to a depth of 6½ inches and put through a 3-mm. sieve, are placed in pots. Enough water is then added to bring the moisture content of the soil to the optimum. The pots of soil are then placed in the respirator and the amount of carbon dioxide evolved determined at various intervals for seven to fourteen days. This method has been used in our investigations.

2. One-kilogram portions of air-dried, sieved soil, taken to a definite depth, are placed in proper containers, adding the necessary amount of water, and the carbon dioxide evolved in forty-eight hours is determined. Stoklasa (28, 29), using only a twenty-four hour period, found that an infertile soil, poor in organic matter, will produce 8–14 mgm. carbon dioxide, a good beet soil produces 56–68 mgm., and a medium soil about 30 mgm.

3. One-hundred gram portions of fresh soil, prepared as for method 1, are placed in 300-cc. flasks with long necks (A in fig. 1). Cotton plugs are placed in the necks of the flasks and in the glass connections. After the proper amount of water is added (50 per cent of total moisture-holding capacity), the flasks are sterilized for 1–1½ hours, on two consecutive days, at 15 pounds pressure. The soils are then inoculated with a culture of a common green *Trichoderma* which was found to be one of the most active groups of soil fungi decomposing celluloses, proteins, pectins and other complex organic substances. The flasks are then connected with the $Ba(OH)_2$ tubes in the respirator and the amount of carbon dioxide evolved is determined for 12–14 days. This method has not been used extensively in the following experiments, but the results obtained are very indicative. Two soils, 5A a fertile soil rich in organic matter, and 7A an infertile soil, poor in organic matter were compared. By this method, 124.08 mgm. and 37.40 mgm. of carbon dioxide respectively were found to be given off in eight days.

The "decomposing power of the soil" can be determined by a group of methods, which differ chiefly in the kind of organic matter added to the soil. A few substances are suggested here, since their decomposition is directly influenced not only by the microbiological activities in the soil, but also by its chemical composition, the presence of available nitrogenous substances and to a lesser extent of phosphates.

1. *Dextrose.* This substance is very readily decomposed in the soil and an excess of material as well as a long period of incubation may obliterate finer differences in the activities of the microörganisms in the different soils. Five hundred milligrams of dextrose was added to 100 gm. of soil. The carbon dioxide evolved was determined every six or twelve hours for a period of 48–72 hours and curves were obtained, which bring out distinctly the differences in the microbiological activities of the different soils. Since dextrose is used very readily as a source of energy not only by the soil fungi and actinomycetes, but also by the great majority of heterotrophic soil bacteria, including the nitrogen-fixing organisms, the rate of decomposition is very rapid. The utilization, by the soil organisms, of all the nitrogen available, during the decomposition of dextrose, will not necessarily stop the production of carbon dioxide. If the nitrogen-fixing organisms are at all active in the soil, they will tend to obtain nitrogen from the atmosphere. In case these organisms fail to develop rapidly and the small amount of nitrogen available is used up, the depressing effect of the limited amount of nitrogen will be registered in the decrease in carbon dioxide production.

2. *Cellulose.* The carbon dioxide evolved from 1 gm. of cellulose added to 100 gm. of soil gives information not only on the "decomposing power of the soil" but also on the amount of available nitrogen and phosphate present in the soil. This is due to the fact that the cellu-

lose is decomposed in the soil (with the exception of alkaline or partially sterilized soils) primarily by fungi.   These rapidly growing organisms consume a great deal of nitrogen in the synthesis of their mycelium and it soon becomes a limiting factor.   The whole question of cellulose decomposition in the soil will be discussed in detail in the following paper of this series.   The distinctive difference in the curves of carbon dioxide evolution from dextrose and cellulose has been pointed out by Dvórák (3).

3. *Rye straw and alfalfa meal.*   One per cent of alfalfa meal has been used extensively in our studies as reported below.   Ordinarily 200 gm. portions of soil were incubated with the organic matter for a period of fourteen days.   Rye straw contains about 0.5 per cent of nitrogen and alfalfa meal about 2.5–3.0 per cent, hence the available nitrogen in the soil may become a limiting factor in the first case, but probably will not in the second.

4. *Dried blood.*   The use of one per cent of dried blood or other organic material rich in nitrogen, such as casein, permits the determination of the "protein-decomposing" capacity of the different soils.   Measurement of ammonia accumulation was not found to be a reliable index of decomposition of organic matter for reasons pointed out elsewhere (35).   Ammonia
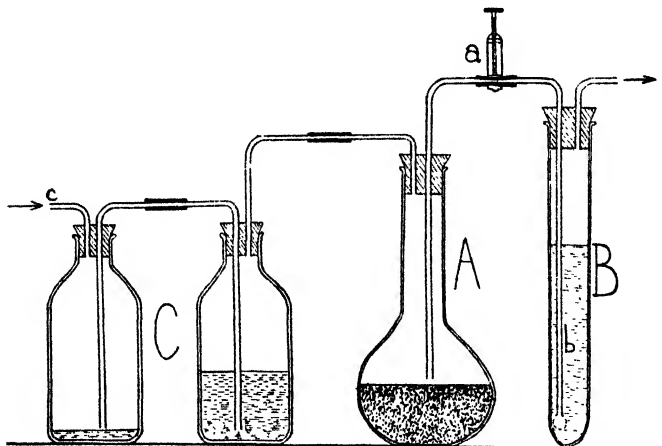
FIG. 1. SMALL APPARATUS FOR DETERMINING THE DECOMPOSING POWER OF SOILS

is an intermediate product in the nitrogen metabolism of a number of organisms and a waste product in the energy metabolism with proteins as a source of energy.   It is, therefore, subject to various changes.   Carbon dioxide, however, is a final product in the energy utilization. That the rates of ammonia and carbon dioxide formation from proteins are very similar is shown by Gainey (6).

APPARATUS

The apparatus which was used to determine the carbon dioxide evolved from the soils in most of the work was not essentially different from that described by Neller (15, 16).   The pots of soil were sealed under bell-jars with paraffin.   Air, freed from carbon dioxide by passage through soda lime and through bottles of 10 per cent sulfuric acid, was then drawn through the bell-jars.   From there the air was drawn through a modified Truog absorption tower (31) containing 50 cc. standard 0.25 N barium hydroxide.   The stream of air was drawn through the apparatus continuously at the rate of three liters per hour for the duration of the experiment except for the intervals when the solutions were titrated.

The source of the suction was a water pump described by Neller (15) which gave a steady uniform suction. The apparatus consisted of two sections: one of six and one of seven units. The excess barium hydroxide was titrated back periodically with 0.25 N oxalic acid to determine the carbon dioxide absorbed, using phenolphthalein as an indicator. The towers were then renewed. One unit of the apparatus was always blank and was used as a control on the appara tus. Any neutralization of the $Ba(OH)_2$ in the tower connected with this unit was considered to be due to the manipulation and at each titration period allowances were made for this control on all titrations of the $Ba(OH)_2$ from the units containing soils. Ordinarily only very slight corrections were necessary. Six differently treated soils were run in duplicate at one time.

A smaller apparatus was devised for determining the decomposing power of soils. Part of one unit is illustrated in figure 1. The long-neck, flat-bottom flask A of 300-cc. capacity took the place of the respiration chamber which in the apparatus described was a bell-jar mounted on a wooden base. The Truog absorption tower was replaced by the 100-cc. test tube B. The bulb at the end of tubing b was perforated with numerous small holes to break up the bubbles of gas. The air, freed from carbon dioxide by passage through soda lime, was distributed to the various units at c and then entered the traps C, containing 10 per cent sulfuric acid. This solution prevented diffusion of the gas from one unit to another. The tubing in the two bottles is so arranged as to keep the solution in the traps in the event of back pressure. The air passed over the soil in the respiration chamber and then through the solution in B which absorbed the carbon dioxide. From B the tubing led to the constant-level siphon water pump.

The respiration apparatus in all cases was enclosed in an incubator room at 25–28°C. The smaller apparatus is less cumbersome than the other and many more units can be run without occupying as much space as the large apparatus.

SOILS USED

Plots of soil from the nitrogen series which have been fertilized alike for fifteen years and used in the previous studies of microbiological methods have also been used in these experiments. A careful record has been kept of the fertilizer applied to the various soils and the resulting crop yields. Although the numbers of microörganisms and nitrifrying capacity of the same soils has been reported previously, the results obtained at the time of sampling for the study of evolution of carbon dioxide are also reported here in order to have a basis for comparison. Ten to twenty-five samples were composited from each plot and put through a 3-mm. sieve.

For the main series of experiments, 1-kgm. portions were placed in glazed earthenware pots of 1-liter capacity. Enough water was added to bring the moisture to optimum which was 50 per cent of the total moisture-holding capacity. To test the decomposing power of the soil, 1 gm. of alfalfa meal was thoroughly incorporated with 200 gm. of soil and enclosed under the belljar respirators in tumblers. The carbon dioxide production from soils treated as in these two cases was determined for 14-day periods.

In determining the production of carbon dioxide by means of the small apparatus, 100-gm. of soil was placed in the flask A and 500 mgm. of dextrose was added in solution and well mixed into the soil. The amount of solution added was sufficient to bring the soil moisture content to optimum. When dextrose was used the production of carbon dioxide was measured at six-hour or twelve-hour intervals for 48–72 hours.

With the large apparatus only duplicate determinations were made with each soil. It was found, however, that the results checked up very well. When some organic matter (alfalfa meal) was added for the study of the decomposing power of the soil, discrepancies were often obtained between duplicate determinations, due probably to the uneven distribution of the added material. The simplified apparatus will permit the making of more than 2 determinations for each soil.

Results

The treatment of the plots, crop yields,[2] nitrfying capacity and numbers of microörganisms are given in table 6. The results on the respiratory power of the soil and on the decomposition of alfalfa meal and dextrose are given in tables 1–5.

The annual fertilizer applications per acre made to the soils used in these experiments are as follows:

PLOT NUMBER	FERTILIZER TREATMENT
5A,* 5B	Minerals,† 16 tons cow manure
6A	Minerals, 16 tons horse manure
7A, 7B	Untreated
9A	Minerals, 320 pounds $NaNO_3$
11A, 11B	Minerals, $(NH_4)_2SO_4$ equivalent to 320 pounds of $NaNO_3$
19A	Minerals only

* The plots marked A are unlimed; those marked B receive two tons of ground limestone every 5 years.

† Minerals = 640 pounds acid phosphate and 320 pounds of muriate of potash per acre.

The results on the respiratory power of the soil as determined by our own method, namely from one kilogram of fresh sieved soil, brought to optimum moisture and incubated for fourteen days, are given in table 1. The respiratory power of the soil, by the same method, but only during the first forty-eight hours of incubation is given in table 2. The results presented in table 2 are comparable with those of Stoklasa, who allowed the soil to air-dry, then added moisture and determined the evolution of carbon dioxide in twenty-four hours. In our experiments, fresh sieved soil was used, since it was found that air-drying produces decided physical, chemical and biological changes in the soil. A two-day period of incubation is preferable since twenty-four hours may not be, in some cases, sufficient to free the chamber from all the carbon dioxide.

The results obtained from the two- and fourteen-day periods of incubation are quite comparable. The manured soils (5A, 6A, 5B) lead by far in the

amount of carbon dioxide formed, which we would naturally expect, since these soils are much richer in organic matter than the other soils, as indicated by their carbon and nitrogen content (table 6). The limed soils (5B) produced somewhat more carbon dioxide than the corresponding unlimed soil, which would tend to confirm the various observations that lime stimulates the decomposition of organic matter in the soil. Nearly one hundred milligrams of carbon dioxide were given off by the unlimed and more than one

TABLE 1

Respiratory power of soils

PLOT NUMBER	CO_2 PRODUCED FROM 1 KGM. SOIL IN 14 DAYS, BEGINNING AT VARIOUS DATES					AVERAGES
	4–11–22	7–10–22	8–18–22	4–3–23	6–26–23	
	mgm.	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*
5A	1327.07		855.81	1159.96	653.23	999.02
6A		1100.75	1160.37			1130.56
7A	155.60	290.16	254.01	244.04	260.02	240.77
9A			499.05	459.41		479.23
11A	551.98	356.15	358.65	354.48	470.26	418.30
19A			423.27			423.27
5B	1425.28				774.85	1100.07
7B	443.96	337.38		517.95	655.16	488.61
11B	666.37	387.60		459.42	578.94	523.08

TABLE 2

Respiratory power of soils

PLOT NUMBER	CO_2 PRODUCED FROM 1 KGM. SOIL IN 48 HOURS, BEGINNING AT VARIOUS DATES					AVERAGES
	4–11–22	7–10–22	8–18–22	4–3–23	6–26–27	
	mgm.	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*
5A	237.24		175.17	206.52	169.91	197.21
6A		182.86	210.82			196.84
7A	21.29	46.93	51.43	36.96	62.33	43.79
9A			122.14	88.27		105.21
11A	74.11	71.25	71.77	58.69	113.23	77.81
19A			90.32			90.32
5B	279.84				215.03	247.44
7B	80.63	66.24		95.65	201.56	111.02
11B	113.42	69.39		79.42	193.30	113.88

hundred milligrams by the limed soil in twenty-four hours. This is more than Stoklasa obtained (68–76 mgm.) for his most fertile sugar beet soils.

The lowest amount of carbon dioxide was produced by the unmanured, unfertilized and unlimed soil 7A, both in two days and in fourteen days. About 22 mgm. of carbon dioxide was given off the first day, which makes it somewhat more than what Stoklasa found in the case of very poor soils. The crop yields reported in table 6 will substantiate the fact that this is the

poorest soil while 5A, 6A and 5B are the most fertile soils in the series. It is important to note the very interesting correlation not only between the respiratory power of these soils with crop productivity but also with numbers of bacteria and nitrifying capacity, as reported in detail elsewhere (34, 36) and as shown in table 6.

Plot 11A has received yearly application of minerals and ammonium sulfate and that has become so acid that it does not support good crop growth; this plot showed a somewhat greater respiratory power than plot 7A. Here again, both two- and fourteen-day periods give comparable results and there is a definite correlation between the respiratory power and crop productivity. The plot receiving minerals only (19A), without any nitrogenous fertilizer or lime comes next to the ammonium sulfate plot in the respiratory power, but is higher in crop yield. This is possibly due to the fact that 11A supports a very abundant fungous flora, while conditions are not favorable for the growth of higher plants. The respiration of the fungi as well as the abundant growth of *acetosella* on 11A probably accounts for the somewhat greater evolution of carbon dioxide than would correspond to its crop production.

The plot receiving sodium nitrate and minerals (9A), the plot receiving lime only (7B) and the one receiving ammonium sulfate, minerals and lime (11B) follow in increasing order of their respiratory capacity. These plots merely show a general parallelism between the respiratory power, crop growth and other biological activities, but not as perfect as in the case of 5A or 7A. This is due to the interfering influence of liming. The addition of lime to an acid soil makes conditions more favorable for the activities of microorganisms, thus resulting in an increase in the numbers of bacteria (decrease of fungi) and an increase in the respiratory power of the soil. This is also accompanied by a greater liberation of plant food and increased crop yield. However, the two may not necessarily correspond, i.e. conditions may be made more favorable for the growth of microorganisms than for the growth of plants. This accounted, in the nitrification studies, for the greater stimulus of lime application to nitrification than to the growth of timothy. The respiratory power is increased somewhat less than the nitrifying capacity so that the results on the respiratory power both in unlimed and limed soils show a closer parallelism with crop yields.

The results on the decomposing power of the soil, when alfalfa is used as a source of organic matter are given in table 3. Here also, decided differences in the capacity of the soils to produce carbon dioxide correspond to their fertility; however, there is no pronounced parallelism. Alfalfa is decomposed in the soil by various groups of microörganisms, especially by fungi. The two poorest soils, 7A and 11A, are distinctly acid in reaction and have, probably as a result of that, an abundant fungous flora, especially 11A. When alfalfa is added to the soil, the fungi rapidly attack the fresh organic matter and a great deal of carbon dioxide is evolved. This will in part compensate for the otherwise lower microbiological activities of these plots in

comparison with the more fertile plots, especially those receiving manure or lime. For this reason, the power of the soil to decompose alfalfa is not considered a valuable index to the respiratory power, and the results are, therefore, not included in the summary shown by table (6).

Decomposition of dextrose as measured by the evolution of carbon dioxide gave results comparable with those obtained in the study of the respiratory power of the soil. However, the length of the incubation period should be short.

TABLE 3

Decomposing power of soils

PLOT NUMBER	CO₂ PRODUCED IN 7 DAYS, BEGINNING AT VARIOUS DATES					AVERAGES
	4-26-22*	7-24-22*	9-1-22*	4-17-23†	7-11-23†	
	mgm.	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*
5A	706.22		601.72	924.32	782.02	753.57
6A		596.84	613.69			605.27
7A	419.14	431.21	455.27	628.11	586.03	503.95
9A			589.82	684.91		637.37
11A	477.59	453.28	467.47	579.70	622.42	520.09
19A			559.04			559.04
5B	621.51				874.46	747.99
6B		603.84				603.84
7B	490.42	539.62		714.77	807.06	637.97
11B	474.13	546.69		699.43	802.10	630.59

* 1 gm. alfalfa meal added to 200 gm. soil.
† 1 gm. alfalfa meal added to 1 kgm. soil.

TABLE 4

Course of evolution of CO₂ from dextrose

PLOT NUMBER	PRODUCTION OF CO₂ IN 200 GM. SOIL TREATED WITH 0.5 GM. DEXTROSE, AFTER VARYING PERIODS OF INCUBATION			
	24 hours	48 hours	72 hours	96 hours
	mgm.	*mgm.*	*mgm.*	*mgm.*
5A	239.03	328.45	376.78	407.17
7A	53.83	147.88	260.45	327.01
7B	139.48	287.93	362.30	389.79

The carbon dioxide produced from 500 mgm. of dextrose added to 200-gm. portions of three soils of distinctly different fertility (5A, 7A and 7B) may serve as an index for differentiating these soils after 24, and even 48 hours of incubation (table 4). On prolonging the period of incubation, the differences gradually disappear. This is again due to the fact that all soils harbor organisms capable of decomposing dextrose, which organisms develop abundantly in all soils with prolonged incubation. This method depends upon the fact that the soil supporting the most abundant microbiological flora before treatment will effect the most rapid decomposition of the dextrose, particularly

during the first two days after its addition. Table 4 indicates the desirability of using a short period of incubation (24–36 hours) when dextrose is used. For this experiment the soils were sampled in the spring. In midsummer and in the fall, the same method indicated diminished production of carbon dioxide from dextrose per unit time, as shown in table 5. Whether this is due to changes in the physical and chemical conditions of the soils or merely their normal variability is not clear. The production of carbon dioxide for forty-eight hours seemed to bring out the greatest differences between the soils.

The amounts of carbon dioxide evolved from the soils from dextrose (decomposing power) are somewhat parallel to the carbon dioxide produced from the soils themselves (respiratory power), as well as to the crop productions

TABLE 5

CO₂ production from soils treated with dextrose

PLOT NUMBER	AMOUNT PRODUCED IN 48 HOURS FROM 100 GM. SOIL TREATED WITH 500 MGM. DEXTROSE			AVERAGES
	7–18–23	9–12–23	10–17–23	
	mgm.	*mgm.*	*mgm.*	*mgm.*
5A	248.76	162.39	175.65	195.60
7A	64.81	31.63	45.15	47.20
9A		91.99	78.60	85.30
11A	190.96		130.73	160.85
5B	304.19	215.20	159.67	226.35
7B	167.58	98.32	112.26	126.05
11B	184.37	96.94	113.30	131.54

and other biological activities (table 6). The two manured soils were most active, the limed (5B) more so than the unlimed (5A). The unmanured and unlimed soil (7A) was least active, and the soils receiving artificial fertilizers and lime were intermediate. Soils 11A and 9A were tested only twice, and, in view of the fact that the actual amounts of carbon dioxide in the different periods of examination were different, a comparison of the averages of the results from 11A and 9A, on the one hand, with the general averages of the rest of the soils, on the other, might not be justified. For this reason, the carbon dioxide production of these two soils from dextrose are not included in figure 2. The relatively larger amount of available nitrogen in soil 11A brought about by the yearly addition of (NH₄)₂SO₄, which is neither used up by the plants nor readily nitrified, as well as the great abundance of fungi probably account for the relative active carbon dioxide production from dextrose in this soil.

Comparisons between crop yields, numbers of microörganisms, nitrifying capacities, respiratory capacities and decomposing capacities of the different soils are given in table 6, and they are graphically represented in figure 4.

The courses of carbon dioxide evolution from 1 kgm. of the soil itself, and in the presence of added organic matter in the form of alfalfa meal based on the average of several different determinations, are given in figure 3.

In plotting figure 4, comparative numbers are used and the data are calculated with the highest figure in each set of determinations being taken as 100. In interpreting these results, it should be kept in mind that a microbiological analysis of a soil would indicate its present crop producing power without further fertilization. It should also give information as to the need of the soil for certain specific fertilizers, organic matter or lime. Of the soils studied,

TABLE 6

Chemical and biological conditions of the soils and their crop productions

| PLOT NUMBER | TREATMENT | REACTION OF SOIL | NITROGEN CONTENT | CARBON CONTENT | TOTAL CROP YIELD PER ACRE | | NUMBERS OF MICROORGANISMS PER GRAM | NITRIFYING CAPACITY† (NO₃-N) IN 100 GM. OF SOIL) | CO₂-PRODUCING CAPACITY | |
					1908–1922	1923 (Corn)			Respiratory (from 1 kgm. of soil in 14 days)	Decomposing (from 200 gm. of soil + 0.5 gm. dextrose in 48 hours)
		pH	*per cent*	*per cent*	*lbs.*	*lbs.*	*thousands*	*mgm.*	*mgm.*	*mgm.*
5A	Minerals + manure	5.5	0.1463	1.73	69,300	6,108	13,040	8.86	999.02	195.60
7A	Untreated	4.9	0.0826	0.96	15,464	1,710	5,600	2.08	240.77	47.20
9A	Minerals + NaNO₃	5.8	0.0994	1.17	57,968	5,273	9,600	6.62	479.23	85.30
11A	Minerals + (NH₄)₂SO₄	4.4	0.1064	1.23	41,754	1,753	5,300	2.16	418.30	160.85
5B	Minerals + manure + lime	6.7	0.1428	1.74	59,754	6,478*	12,500	12.07	1100.07	226.35
7B	Lime only	6.5	0.0868	1.18	30,160	5,566	9,800	7.87	488.61	126.05
11B	Minerals + (NH₄)₂SO₄ + lime	6.1	0.0952	1.10	61,906	6,440*	10,600	8.75	523.08	131.54

* Actual yield of corn grain was less in 5B than in 5A and was about the same in 11B as in 5A.

† See Waksman (36).

5A and 5B are seen to be the most fertile and 7A the least fertile. The actual crop production of these is actually correlated with the results obtained from a microbiological analysis. Soil 5A produced a larger crop yield during the 15-year period than 5B, but the yield of corn in 1923 was higher in 5B than in 5A. The numbers of bacteria are higher in 5A than in 5B, while the respiratory and decomposing powers, especially the latter, are higher in 5B; the nitrifying capacity of 5B is even still higher than of 5A. The reaction of 5B which is probably more favorable for the activities of the nitrifying bacteria and nitrogen fixing bacteria, is probably responsible for these differences.

The data for 7A are quite parallel, except for the numbers of microörganisms which appear higher than the other data. Here again, nitrification, crop yield, respiratory and decomposing powers are correlated.
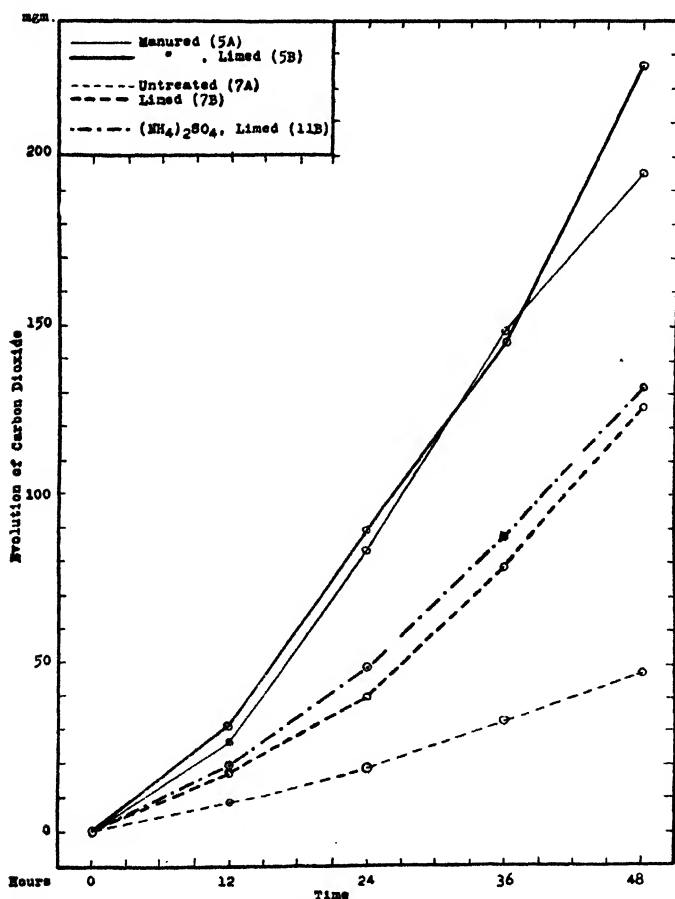
FIG. 2. COURSE OF CARBON DIOXIDE PRODUCTION FROM DEXTROSE ADDED TO SOILS OF DIFFERENT FERTILITY

The addition of lime to a soil which has been cultivated for 15 years, without any additional fertilizers (7B) greatly increased the crop yield.   This may be due to the reaction (pH = 6.5) which favors the activity of the nitrogen-fixing bacteria, as will be shown in a subsequent contribution.   The reaction also affects the other microbiological activities, the nitrifying and oxidative capacities and especially the number of microörganisms.   The comparatively
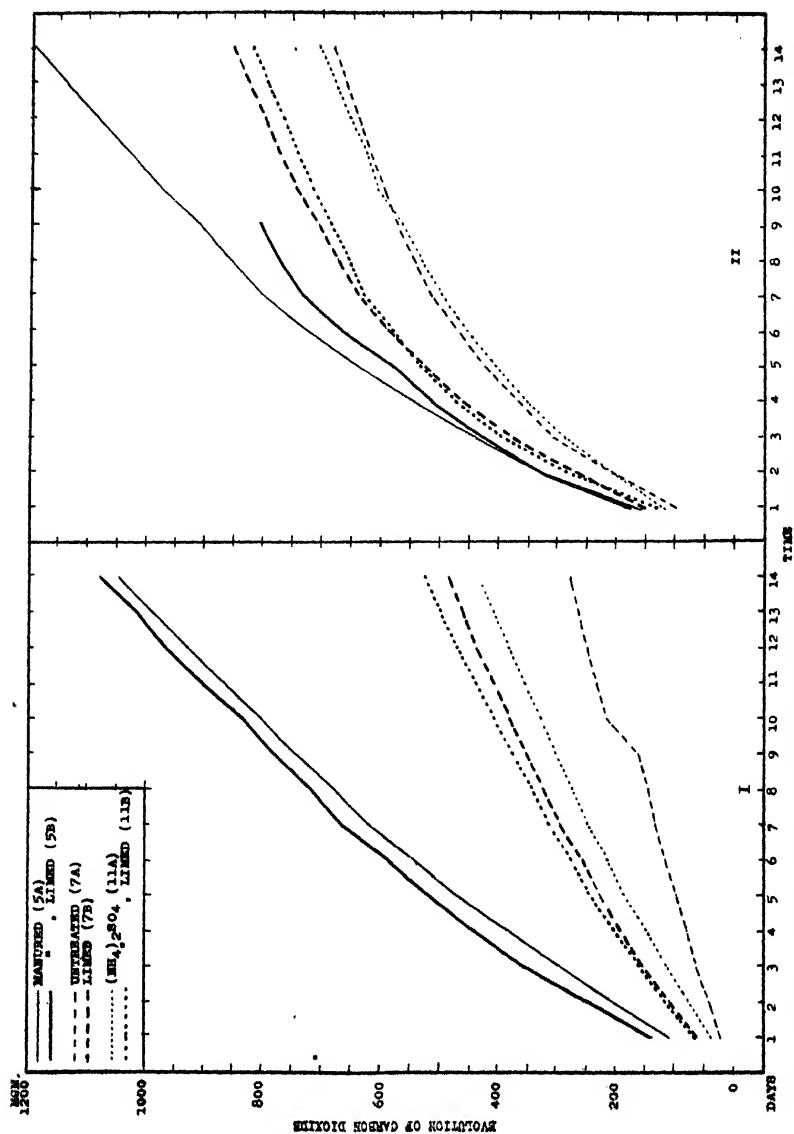
FIG. 3. EVOLUTION OF CARBON DIOXIDE FROM FRESH SOILS OF DIFFERENT FERTILITY WITHOUT FURTHER TREATMENT (I); AND IN PRESENCE OF 0.2 PER CENT ALFALFA MEAL (II)
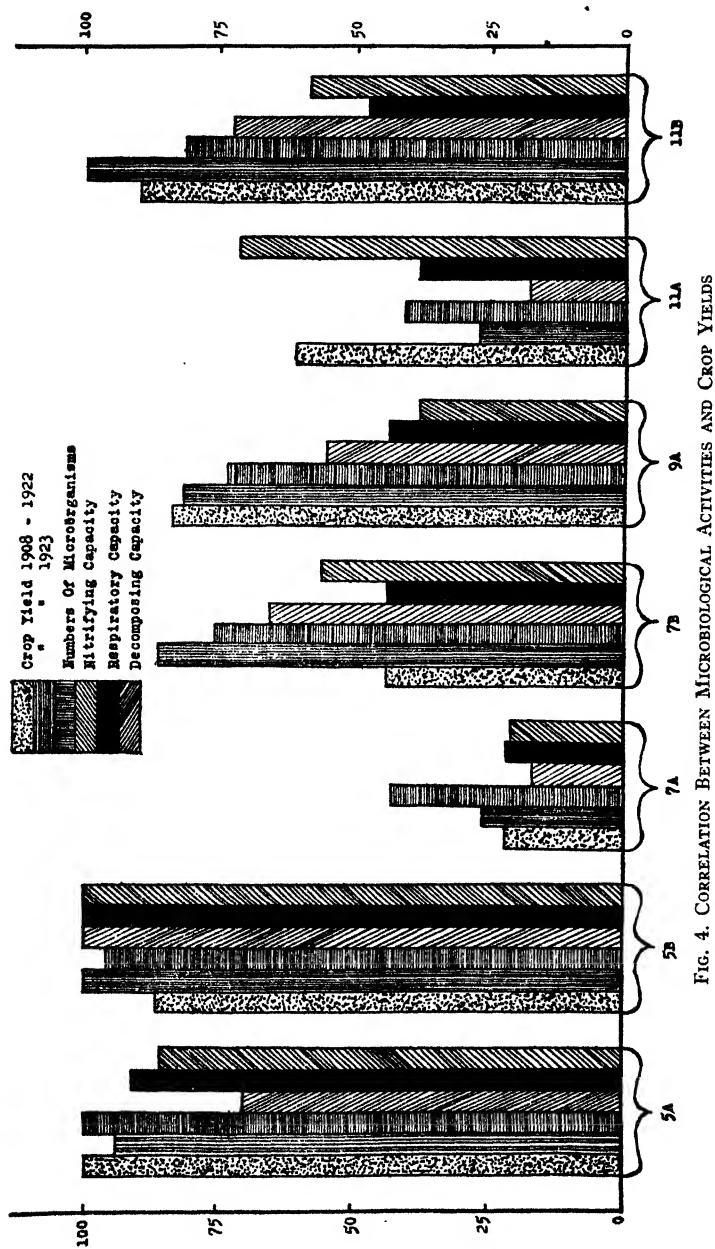
FIG. 4. CORRELATION BETWEEN MICROBIOLOGICAL ACTIVITIES AND CROP YIELDS

low respiratory power of this soil is caused rather by the low content of the available organic matter than by microbiological inactivity. It is interesting to note that although the carbon contents of 7A and 7B are almost the same, the respiratory power, or the amount of carbon dioxide produced by 1 kgm. of soil kept for fourteen days under optimum conditions, is nearly twice as high in 7B than in 7A. This serves also to emphasize the fact that it is not sufficient to determine the respiratory power of a soil as a measure of its capacity to produce carbon dioxide from the viewpoint of microbiological methods, but it is also necessary to determine the relative rapidity with which these solids decompose readily available sources of energy, like dextrose.

The fact that the mere use of inorganic fertilizers, without stable manure, green manure or lime will not work towards the formation of a soil supporting any active microbiological flora is brought out clearly in the results from soil 9A. Although the total crop yield has been kept very high, comparatively low numbers of microörganisms and especially the low nitrifying, respiratory and decomposing powers seem to indicate that the soil is not as active biologically in comparison with the crop yields as are the other soils. The fact that the respiratory and decomposing powers of a soil obtaining artificial fertilizers, as in the case of 9A, are not as high as its crop yield need not necessarily mean that these microbiological activities cannot serve as indices of soil productivity. These two factors—microbiological activity and soil productivity—need not of necessity be related. The one, crop production, is at any moment dependent to a large extent upon the inorganic nutrients present of the soil, while the other, microbiological activity, is regulated to a much larger extent by the abundance of soil organic matter. A soil composed of little else than quartz sand with available elements essential to plant growth may support plants temporarily and still lack any abundant microbial flora. In such cases the *microbiological activities* and *soil productivity* are not correlated but the first *may be better considered as forecasting the future possibilities of the soils.* So with these studies an abundant microbial life may better be considered to indicate that the soil has been built up to a state of fertility which is more permanent than when the microbial activity is considerably less. Although the two may not be correlated at any one time they both approach the same limit.

Similar results are obtained in the case of the soil receiving ammonium sulfate and lime (11B). In this case, the crop yield for 1923 was higher accompanied by a more abundant microbial flora, greater nitrifying and oxidative powers. Since the carbon content is about alike in both plots and the soil reaction is nearly alike, we would expect about the same respiratory powers. As a matter of fact, 11B, with a somewhat lower carbon content, has a somewhat higher respiratory power, corresponding to the better microbiological activities.

Soil 11A is abnormal; the continued use of ammonium sulfate resulted in a great increase in acidity (pH 3.9 to pH 4.4) and an abundant fungous flora.

The added nitrogen is not taken away by the plants and a part of it is prob-
ably present as absorption compounds of the zeolitic silicates and a part in
the fungus mycelium. The crop yield has been constantly decreasing till in
1923 it is as low as in 7A, the soil receiving no fertilizer. The comparatively
low numbers of bacteria, low nitrifying and respiratory powers go hand in
hand with the low crop yield. However, the decomposing power of this
soil is very high, probably due to the decomposition of the dextrose added,
by the abundant fungus flora in the presence of the available nitrogen.

SUMMARY

Determination of the amounts of carbon dioxide evolved from the soils,
both without and with the addition of small amounts of organic matter, can
be used in grading these soils on the basis of their fertility as well as can
determinations of the numbers of microörganisms and nitrification in the soils.
The data presented in this paper together with those published previously on
the microbiological analysis of soils allow us to look forward to the devel-
opment of a group of quantitative methods for determining the productive
capacity of the soil.

To measure the capacity of the soil to produce carbon dioxide, two methods
are suggested: One, determining the amount of carbon dioxide formed from
one kilogram of fresh soil, for fourteen days under optimum conditions of
temperature and moisture; two, determining the amount of carbon dioxide
produced from 500 mgm. of dextrose added to 100 gm. of fresh soil, in forty-
eight hours.

Soils rich in organic matter produce by far the greatest amount of carbon
dioxide (this does not apply to peats, mucks or such abnormal soils). The
amount of carbon dioxide produced is not, however, proportional to the
carbon content of the soils. The addition of lime to an acid soil stimulates
the production of carbon dioxide, but not to as great an extent as nitrification.
This is due to the difference in the nature of the organisms responsible for
the chemical changes.

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THE QUANTITATIVE DETERMINATION OF NITRATES IN SOIL

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METHODS IN USE

Many methods have been devised for carrying out this important determination; some give very reliable results under particular circumstances only, while others are of doubtful merits and are quite inapplicable when very small quantities of nitrates are under consideration.

Of the more common methods Grandval and Lajoux's phenoldisulfonic acid method is perhaps the best known. One modification of the method is described in full by Fraps, (12, p. 10–12) and it appears to be used very extensively. But very serious objections have been raised against its use when applied to soils containing appreciable amounts of salts (4). Chlorides especially interfere very much (30). Organic matter also vitiates the results (27, 33) obtained by its use. In order to make the method more general, modifications have been introduced by various workers, among whom may be mentioned, Perrier and Farcy (25), Syme (33), Farcy (11), Caron and Raquet (7), Chamot, Pratt and Redfield (8), Gericke (14), Nichols (23), Frederick (13), and Noyes (24). The method is therefore unreliable unless by preliminary work on the soil we find out what particular precautions should be taken. Moreover, as it is sometimes necessary to add a flocculating agent when obtaining the soil solution, further complications are introduced. Other colorimetric methods suffer from the same drawbacks.

It is sometimes necessary to estimate very small quantities of nitrates. In such cases all gasometric methods of estimation are inapplicable, as the unavoidable experimental errors become relatively too large. The impracticability of carrying out a large number of determinations at the same time and the cost of apparatus further militate against their use.

Busch (5) has devised a gravimetric method for estimating nitrates. Nitrates form an insoluble compound with "nitron" (diphenyl-endanilo-dihydro-triazole) in the presence of acetic acid. The method gives very accurate results when pure nitrate solutions are employed. But it breaks down in the presence of certain acids, salts and other substances found in the soil, since it also forms insoluble compounds with these. The crystallization of the insoluble nitrate compound is also interfered with when much organic matter is present. Some of these difficulties are discussed by Litzendorff (20). Even under the most favorable circumstances as far as extraneous matter is concerned, it is unreliable when the amount of nitrate is very small, since the experimental error introduced by washing and weighing becomes too great. The cost of the nitron is often prohibitive when a large number of determinations have to be done. The method as applied to pure nitrate solutions and also in the case of some mixtures has been rigorously investigated by Collins (9).

In a large number of methods the underlying principle is the reduction of the nitrates to ammonia, and the subsequent estimation of the ammonia. The best known of the methods belonging to this group are the zinc-copper couple method, the Ulsch acid reduction method, the Devarda alkaline reduction method, and the aluminum alkaline reduction method.

Objections have been raised against all these methods, and modifications have been introduced in some cases in order to overcome the difficulties encountered.

Purvis and Courtauld (28) have shown that the presence of albuminous matter interferes with the accuracy of the zinc-copper couple method. The nitrates are sometimes not completely reduced, while in other cases ammonia is formed from the organic matter present. The time and labor required in the preparation of the couples makes the method unsuitable when a large number of determinations are to be carried out simultaneously.

The Ulsch (34) acid reduction method is strongly recommended by Greaves and Hirst (15). Burgess (4) finds difficulties of technique in it, which, in the case of numerous determinations, would render the method impracticable. A critical examination of the method will be found further on in this paper.

In the Devarda method (10) an alloy of aluminum, copper and zinc is used, and the reduction is carried out in alkaline solution. Here again modifications had to be introduced. Allen (1) claims that the accuracy of the method as modified by him is limited only by the unavoidable error attaching to the measurement of the standard solutions. Russell (29) describes further improvements. Whiting, Richmond and Schoonover (37) substitute sodium peroxide for the hydroxide. Many of these improvements make the determination too involved or require special apparatus and are, therefore, unsuitable when several nitrate determinations are to be carried out together. Cahen (6) has shown that very reliable results are to be obtained when pure nitrate solutions are under consideration. Mitscherlich (22) finds the reduction complete when carried out in strongly alkaline solution. According to Greaves and Hirst (15) organic matter interferes in the method.

We have not been able to find any information about the applicability of the Devarda method to determinations of very small amounts of nitrates. The titration of the ammonia produced seems to be the general practice. In soils containing only about two parts per million of nitric nitrogen very large amounts of the soil have to be extracted, which will in general be extremely inconvenient, or else the unavoidable error of titration will make the determination worthless. To take an example, let the extract equivalent to 250 gm. of soil containing 2 parts per million of nitric nitrogen be reduced and the ammonia evolved collected in standard 0.1 N acid. One cubic centimeter of this acid is equivalent to 1.4 mgm. of nitrogen and the total nitrogen under consideration is only 0.5 mgm. We shall therefore have a titration of less than 0.4 cc. The relative magnitude of the experimental error is obvious.

The aluminum reduction method described by Burgess (4) is simple to carry out, and requires no special apparatus or reagents. He has shown it to be very reliable under a number of varying conditions which are likely to occur when working with soil solutions. He has applied it to solutions in which the amount of nitric nitrogen is relatively large and titration with 0.1 N acid could be resorted to. The reduction was practically complete. The author of this paper has successfully applied the method, with certain modifications, to the estimation of very small quantities of nitrates, where it was necessary to Nesslerize the ammonia produced. A large number of duplicate determinations were done by the modified method, as described in full further on in this paper, and very satisfactory results were obtained.

A discussion of the above methods and other methods in use, together with a long list of references, is given by Greaves and Hirst (15) in their paper entitled "Some factors influencing the quantitative determination of nitric nitrogen in the soil."

METHODS OF EXTRACTION

In every investigation on the amount of nitric nitrogen in a soil it is necessary in the first place to obtain a solution of this nitrate, so that it may be separated from the bulk of the soil. Many methods of obtaining this soil extract are in use, but none are ideal and some are quite useless when the nitrate is subsequently determined colorimetrically.

Organic matter interferes in most of the methods, and it is therefore desirable to have the soil extract free from it. The Pasteur-Chamberland filter gives a clear solution (31). But

it occasions slight losses of nitrates (2, p. 31).   The time factor when working with heavy soils will be very variable and where a long time is taken for filtration changes in the nitrate content are likely to occur on account of bacterial activity, even if the filter is thoroughly cleaned and sterilized before each filtration.

The centrifuge was tried on soils rich in soluble salts and having a high clay or organic colloid content by Hirst and Greaves (16).   They found that some solutions were not clear after 30 minutes centrifuging.

Suitable flocculating agents have therefore been resorted to.   There exists a great divergence of opinion about the efficacy of some of these substances.   Among the more common flocculating agents there are aluminum sulfate, aluminum chloride, ferric sulfate, sodium chloride, hydrochloric acid, potassium alum, iron alum, sodium alum, calcium carbonate and lime.   Sulfates, chlorides, hydrochloric acid and aluminum and iron salts may not be used when the nitrate is subsequently determined colorimetrically.   Where lime is used together with chloroform as an antiseptic, the colorimetric method also fails.

Greaves and Hirst (16) consider potassium alum the most suitable flocculating agent.   The flocculating power of twenty-two common acids and salts on a highly puddled Hawaiian clay soil was investigated by McGeorge (21).   He found aluminum sulfate to be the most active substance.   The divalent calcium and magnesium salts of nitric, hydrochloric and sulfuric acids are next, while the monovalent salts of sodium, potassium and ammonium are least active.   The acids are stronger than any of their divalent salts but the trivalent salt, aluminum sulfate, is stronger than any of the acids.

Potter and Snyder (26) use calcium carbonate as flocculating agent and prefer it to calcium oxide.   Burgess (4) uses lime and gets practically complete recovery of nitrates.   Wolkoff (39) found aluminum compounds the most suitable for flocculating clay.   Lipman and Sharp (19) recommend the use of quicklime, and state that the use of 2 gm. of CaO to 100 gm. of soil gave the whole of the nitrate nitrogen in a soil of known nitrate content.

Noyes (24) recommends the use of calcium hydroxide as being the best precipitant of colored organic matter.   Dilute hydrochloric acid (approximately 0.5 per cent) is used as a settling agent by Whiting, Richmond and Schoonover (37).   Whiting and Schoonover (38) state "a large number of substances such as water, alkalies, alkaline earths and other carbonates, oxides, neutral salts, and various acids have been tried for securing an extract, but the results have shown hydrochloric acid to be the best deflocculating and settling agent as well as a superior agent in assisting in freeing the nitrate."

The other factors to be taken into consideration in obtaining the soil extract are the amount and condition of the soil, the ratio of soil to water, and the time of extraction.   Here also we find a great divergence in the methods adopted by different workers.

Burgess (4) takes 100 gm. of the soil in an enamelled cereal dish, 2 gm. of powdered CaO and 200 cc. of water are added.   The contents are thoroughly ground and mixed with a pestle for 3–5 minutes, after which the soil and clay are allowed to settle for 15 to 20 minutes, and the solution then filtered through paper.

Whiting and Schoonover (38) take 70–80 gm. of the oven-dried sample which had been placed in a 400-cc. shaker bottle.   They add 300 cc. of hydrochloric acid (approximately 0.2 per cent) and shake in a mechanical shaker for 3 hours.   The mixture is allowed to settle overnight.

Stewart and Peterson (32), working on the nitric nitrogen of the country rock, place 100 gm. of the finely ground rock in a large bottle with 1000 cc. distilled water, and shake for 16 hours in a shaking machine.   The solution is then separated through a Pasteur-Chamberland filter.

Kelly (17) takes 200 gm. of dry soil in a flask; 500 cc. of water are added, and the flask is then vigorously shaken once every ten minutes for an hour and then filtered through a Pasteur-Chamberland filter.   ·

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Noyes (24) takes 50 gm. of soil and shakes for a minute with 200 cc. water. The mixture is shaken again after half an hour, and again after another half hour. Five grams of CaO is sometimes added before the 200 cc. water, if there is a probability of the solution not being clear.

Wahnschaffe (35) adds 2000 cc. water to 1000 gm. of fine air-dried soil, and shakes for 48 hours.

Buhlert and Fickendey (3) have investigated the influence of the time of shaking and the amount of water on the nitrate determination, as well as the difference produced when the soil is air-dried, or oven-dried at 100°C. They suggest drying the soil at 60–70°C. since bacterial activity ceases at 55°C. They found that shaking three times during 10 minutes was not sufficient to give all the nitrate. But 20 minutes shaking gave the maximum. They also recommend the addition of 2 per cent sodium chloride to clarify the extract. Two kilograms of soil together with 2–3 liters of water should be shaken for a $\frac{1}{4}$ minute at intervals of 5 minutes, and the process continued for 30 minutes.

Russell (29) dries at 55°C. and takes 200–500 gm. of the dried soil, and presses it firmly in a Büchner funnel fitted to a filter flask. Water is poured over the surface of the soil and the filtrate collected. At least 300 cc. should be collected for the nitrate determination. He considers that nearly all the nitrates are washed out by the first 300 cc. of filtrate.

Greaves and Hirst (15) have concluded that nothing is to be gained by shaking 100 gm. of soil with 2 gm. of alum and 500 cc. water longer than 5 minutes in a mechanical shaker. They qualify their statement however by saying "It must be borne in mind that these tests

TABLE 1

Nitric nitrogen in soil

	WITHOUT PREVIOUS DRYING	AFTER DRYING AT 58–63°C.
	p.p.m.	*p.p.m.*
a	14.45	16.78
b	14.31	16.90
Average............ ...	14.38	16.84

were carried out on finely powdered soil and not upon lumps." We could not find out exactly what was meant by "finely powdered soil." They have also investigated the effect of different ratios of soil to water on the nitrate determination, and conclude that the ratio is immaterial, provided there is not sufficient nitric nitrogen present to give a saturated solution.

Whenever the process of extraction takes some time there is the danger of bacterial activity changing the amount of nitrate. The use of an antiseptic then becomes desirable. Chloroform is probably the most common one in use. Greaves and Hirst (15) have investigated this point, and they conclude that there is very little danger of a change in the nitrate content taking place during the first few hours after adding the water for extraction. If 2 gm. of alum have been used as flocculating agent they consider no other antiseptic necessary, unless the solutions are to remain several hours, when 0.5 cc. chloroform will be sufficient to inhibit all bacterial activity.

It only remains to be added that special precautions must be taken when soil samples are taken in which nitrates are to be determined. Russell (29) states that the samples must be dried without any delay at 55°C. Even then a change of the nitrate content can take place in some soils. We have taken a sample of moist soil, and by duplicate determinations have obtained the amount of nitrate present in a uniform portion of it with the least possible delay, without previous drying. The remaining portion was weighed and dried for 18 hours as soon as possible in an oven at a temperature of 58–63°C. It was weighed again, and from

the results the amount of moisture calculated. Nitrates were determined in this dry portion. On calculating the amount of nitrates in the wet portion to the dry basis the results given in table 1 were obtained.

We thus see that there is a gain of very nearly 2½ parts per million. These results were obtained with a very heavy soil. The wet sample was therefore of a very lumpy nature. It probably took a long time before 55°C. was reached inside the lumps and in the warm damp soil bacteria probably became very active for a while. This would account for the increase in nitrates.

The determination of nitrates in the average laboratory soil sample which has been left lying in storage without thorough drying is of very doubtful value.

According to Waynick (36) a very large number of samples must be taken even from an apparently uniform area of limited extent in order to give a truly representative sample on mixing. He considers 10 or 16 a very limited number of samples.

THE ALUMINUM REDUCTION METHOD COMPARED WITH THE ULSCH METHOD

Allen (1) contradicts Burgess and states that the aluminum reduction method breaks down utterly in the presence of much organic matter of the type yielded to water by soils. This might be the case if the reduction is carried out in the aqueous extract from which nothing has been·precipitated by lime. But if carried out as done by Burgess on an extract from which most organic matter has been precipitated by lime and filtered, we disagree entirely with Allen. We have done a number of determinations where a known quantity of nitrate has been added to the soil solution, and in every case recovery was almost complete.

Greaves and Hirst (16) state that "Conclusive evidence has been produced to show that when lime is used in the determination of nitric nitrogen by the phenoldisulfonic acid, the aluminum reduction or the Ulsch reduction methods low results are obtained." They refer to Potter and Snyder (26) for the results obtained by the aluminum reduction and to their own figures (15) in the case where the Ulsch method is used. They also state "this is not due to the lime carrying out with the colloid some of the nitrate, for similar results are obtained when lime is added to a pure solution of sodium nitrate and the nitric nitrogen is determined directly by the Ulsch method." In another article (16) they state that lime interferes with the determination of nitric nitrogen and can be discarded.

We have added lime to a solution of pure KNO_3 of known nitrate content, filtered, after shaking up well, and then reduced the nitrate in the filtrate by the aluminum reduction method. The recovery was complete to all intents and purposes, as is shown by table 2.

From general chemical considerations it seems rather strange that lime water should interfere with the estimation when pure solutions are employed. It is to be remembered that Greaves and Hirst (16) recommend the use of alum for flocculation as causing the least loss of nitrates. The conclusive evidence against the use of lime and the superiority of alum carry very little weight when some of their published figures are examined. The following table can be drawn up using the figures given by them (15, p. 184–185). It

must be remembered that each figure given by them is an average of from two to four separate determinations. A heavy clay soil and a greenhouse loam soil with a high percentage of organic matter were used to compare the results obtained by the Ulsch reduction, aluminum reduction and phenol-disulfonic acid methods, using different methods of obtaining a clear solution.

TABLE 2

Nitric nitrogen recovered from solution of KNO₃ by the aluminum reduction method

	TREATMENT OF KNO₃	AMOUNT OF NITRIC NITROGEN ADDED	AMOUNT NITRIC NITROGEN RECOVERED	AVERAGE	AVERAGE RECOVERY
		mgm.	*mgm.*	*mgm.*	*per cent*
a	No CaO added	2.53	2.51	2.46	97.2
		2.53	2.41		
b	4 gm. CaO	2.53	2.69	2.64	104.2
	0.5 cc. CHCl₃	2.53	2.59		

TABLE 3

Effect of flocculating agents on recovery of nitric nitrogen from soil

METHOD	SOIL	NITRIC NITROGEN ADDED TO SOIL	NITRIC NITROGEN RECOVERED	
			CaO as flocculating agent	K-alum as flocculating agent
		mgm.	*mgm.*	*mgm.*
Aluminum reduction method	Heavy clay	....	0.32	0.46
		10	9.49	9.85
	Greenhouse loam	....	2.17	1.61
		10	11.83	11.91
	Totals..........................		23.81	23.83
Ulsch method	Heavy clay	....	0.88	0.70
		10	10.51	10.37
	Greenhouse loam	....	2.52	2.28
		10	12.19	12.12
	Totals...........................		26.10	25.47

From table 3 we see that where the aluminum reduction method is used CaO and potassium alum have practically the same effect if the totals are considered. But with the Ulsch method we find that without exception higher results are obtained where lime is used. If the totals under CaO and potassium alum are taken we find 49.91 mgm. nitric nitrogen recovered where CaO is used, and only 49.30 mgm. where the alum is used. From these figures we might feel inclined to say that potassium alum causes a bigger loss

of nitrate than lime, which is the very opposite of Greaves and Hirst's contention.

It appears however from the above figures that more nitrate is recovered by the Ulsch method than by the aluminum reduction method. A critical examination was therefore made of the tables given by Greaves and Hirst from which the above figures were obtained. They applied the two methods to solutions obtained by nine different ways of clarifying—filter, centrifuge, CaO, CaCO₃, talc, potassium alum, sodium alum, iron alum, and ferric sulfate. Table 4 can be constructed for the two soils on working out the averages of the figures given.

If the results obtained by the Ulsch method are taken as standard and those by the aluminum reduction method compared with them on a percentage basis, we find that the recovery of nitrate by the aluminum reduction method is directly proportional to the concentration of the nitrate. Only

TABLE 4

Average nitric nitrogen recovered from soil

SOIL	NITRIC NITROGEN ADDED TO SOIL	ULSCH METHOD		ALUMINUM REDUCTION METHOD		RECOVERY BY ALUMINUM REDUCTION METHOD TAKING ULSCH METHOD AS STANDARD
		Amount recovered	Number of determinations	Amount recovered	Number of determinations	
	mgm.	*mgm.*		*mgm.*		*per cent*
Clay................ {	.....	0.65	30	0.36	28	55.8
	+10	10.41	30	9.58	28	92.0
Greenhouse loam.......... {	.....	2.48	28	1.93	27	77.7
	+10	12.31	28	11.43	27	93.1

55.8 per cent is recoverable where 0.65 mgm. of nitrogen is reduced while 93.1 per cent is obtained when 12.31 mgm. of nitrogen is reduced. That the reduction should become more and more complete the larger the amount of nitrate to be reduced is against our experience. And from the nature of the chemical reaction it certainly seems extraordinary. We have done a large amount of work which involved the reduction of very small amounts of nitric nitrogen (.25–2.5 mgm.) by the aluminum reduction method, and have found the reduction of such small quantities complete to all intents and purposes, in fact there was a tendency to get rather more than 100 per cent. Such reductions have also been carried out with soil solutions to which a small known amount of nitrate had been added, with the same result. We incline, therefore, to the view that a constant plus error is involved in the determinations of Greaves and Hirst by the Ulsch method. That method which gives the greatest amount of nitrate is not of necessity the most reliable method.

We have tried using alum as a flocculating agent, but found that as much nitrogen was recovered from the blanks as from the solutions from soil treated with nitrates.

In the above discussion we have not considered the corresponding figures obtained by the phenoldisulfonic acid method, where such were given. If any nitrites are present they will behave like nitrates when the reduction methods are employed and will also be reduced to ammonia. But in the direct colorimetric method the nitrites yield a yellow coloration the intensity of which is equivalent to that given by a quantity of nitrate containing one-third of the amount of nitrogen present in the nitrite (27). Kelley (18, p. 432) gives figures showing the wide range of results obtained by the use of different methods when applied to soils containing a high concentration of nitrogenous material. Table 5 is quoted from his paper.

TABLE 5

Effects of nitrite on the determination of nitrate

	NITRITE NITROGEN	NITRATE NITROGEN BY MODIFIED COLORIMETRIC METHOD	NITRATE NITROGEN BY THE USUAL COLORIMETRIC METHOD	NITRATE NITROGEN BY ALUMINUM REDUCTION METHOD
	p.p.m.	*p.p.m.*	*p.p.m.*	*p.p.m.*
Soil plus 1 per cent of dried blood incubated for 46 days..........	275	22	30	283

TABLE 6

Nitric nitrogen obtained from three soils on using different amounts of lime

AMOUNT OF CaO USED	NITRIC NITROGEN RECOVERED		
	Soil A	Soil B	Soil C
gm.	*p.p.m.*	*p.p.m.*	*p.p.m.*
2	2.14 2.16		
4	2.48 2.67	2.48	1.50
5		2.51	1.56

Since we adopted lime as a flocculating agent we considered it necessary to investigate the effect of the quantity of lime used on the amount of nitrate found by the aluminum reduction method. Greaves and Hirst (16) state that when lime is used as a flocculant the quantity of nitric nitrogen recovered is inversely proportional to the quantity of lime added to a soil-water mixture. From the results of our trials we cannot substantiate their statement. Table 6 shows the results of our experiments on this point.

From our results it appears that there is certainly not less nitrate when more lime is used, in fact there is a slight gain. The phenomenon underlying this slight gain is at present being investigated.

MODIFICATIONS INTRODUCED INTO THE ALUMINUM REDUCTION METHOD

An ideal method for estimating nitrate would be one which conforms to the following requirements:

(1) It must be applicable to all cases, so that no preliminary work is necessary on the soil in order to find out whether it can be adopted.

(2) It must give accurate results.

(3) The ordinary equipment of the average laboratory should suffice for the determination, and it should be independent of chemicals difficult to procure.

(4) It must not involve undue time and labor.

Such a method, which gives good results where fairly large quantities of nitrates are involved, is described by Burgess (4). It is very simple to execute, and he has shown it to be applicable in cases where the phenol-disulfonic acid method fails hopelessly. The method, in principle, was adopted by the author in work which involved the determination of small quantities of nitrates in a large number of soil samples.

It had to be modified, however, in order to obtain greater accuracy. The soils on which most of the work was done rarely contained more than 3 parts per million of nitric nitrogen. The titration of ammonia with 0.1 N HCl after reduction, as carried out by Burgess, is therefore not accurate enough. In 50 gm. of a soil containing 3 parts per million of nitric nitrogen there will be after reduction an amount of ammonia equivalent only to about 0.1 cc. 0.1 N HCl. The titration error alone therefore will represent anything from 25–50 per cent of the total amount. And even with the concentrations used by Burgess we find that the figures given by him in the second decimal place are quite worthless, in view of the titration error involved.

It was impracticable to use very much more than 100 gm. of soil for a determination, and it was also impossible in some cases to obtain more than 100 cc. filtrate, out of the 200 cc. water added, in which to determine the nitrates.

We were thus compelled to adopt a colorimetric method for estimating the ammonia produced on reduction. Very consistent results were then obtained, as will be shown further on in this paper.

Since it was sometimes impossible to obtain 100 cc. filtrate when only 2 gm. of CaO was added, as done by Burgess, we used 4 gm. instead. After stirring with 200 cc. water, and filtering, it was then always possible to get at least 100 cc. filtrate.

The process of stirring the soil with water was also abandoned since from some of our results it appeared doubtful whether all the nitrates came into solution in the tedious operation of stirring by hand. Mechanical shaking was resorted to for the following reasons:

(1) There was no chance of any lumps of soil remaining unbroken.

(2) Conditions could be made exactly similar in different determinations, and did not involve the personal factor of stirring.

(3) Duplicate determinations agreed better after shaking than after stirring.

(4) It involved practically no extra work. The time factor was greater, but 0.5 cc. chloroform was added before commencing to shake, in order to eliminate all possibilities of bacterial activity.

On account of the very small amount of nitrate we were working on, we did not investigate the minimum time required for shaking, in order to bring all the nitrates into solution. We therefore adopted an arbitrary period. The sample of soil was shaken with 200 cc. water in the bottle for 90 minutes. This brought about what appeared to be complete disintegration of the aggregates of soil particles; 4 gm. of CaO were then added and the shaking continued for another 30 minutes. After this the mixture was filtered through a ribbed filter paper.

TABLE 7

Effects of area and distribution of aluminum sheets

NATURE OF STRIPS	AMOUNT OF NITROGEN ADDED IN FORM OF KNO₃	NITROGEN RECOVERED	PERCENTAGE RECOVERY
	mgm.	*mgm.*	*per cent*
Small pieces............................	2.5	2.46	98.4
Small pieces............................	5.0	4.84	96.8
Four thin strips........................	2.5	2.38	95.2
Four thin strips........................	5.0	4.72	94.4
Three curls*........................... {	2.5	2.52	100.8 } 101.2
	2.5	2.54	101.6 }
Three curls*........................... {	7.5	7.26	96.8 } 97.9
	7.5	7.41	98.8 }

* Total weight of three curls = 1.2 gm.

The aluminum used in the work consisted of strips cut from thin aluminum sheet. The influence of the area of the strips used and their distribution in the liquid containing the nitrate was investigated with the results shown in table 7. Instead of test tubes, 300 cc. wide-mouthed Erlenmeyer flasks were used since they were easier to manipulate. The strength of the NaOH used was 1 per cent and it occupied a volume of 150 cc. The aluminum was placed in the flasks in the following forms:

(1) One large strip, 1 cm. wide and 9 cm. long cut up into small pieces.

(2) Four thin strips, each 0.25 cm. wide and 18 cm. long.

(3) Three strips, each ½ cm. wide, 15 cm. long, and curled into the form of a rough spiral which just goes through the neck of the flask, and has its parts more or less uniformly distributed throughout the volume of the liquid to be reduced.

The reductions were all done at room temperature. They were started late in the afternoon, and the ammonia formed was distilled off the next morning. The time of reduction was 17–19 hours and the room temperature, 21°–25°C. in summer. On some mornings in winter it was found to be as

low as 14°C. but this did not affect the results, as table 8 shows. This gives a recovery of 99.6 per cent. No use, therefore, was made of an incubator in the determinations.

If the reduction was done in an open flask there was a slight smell of ammonia to be noticed the next morning at the mouth of the flask; it was enough to turn red litmus blue when the moist paper was held over the solution. As the solution was not very alkaline it appeared that some of the ammonia was carried out of the liquid mechanically by the hydrogen evolved. It did not seem that the capillary tube used by Burgess to close off the open end of the test tube would prevent the escape of the ammonia as it was carried forward

TABLE 8

Recovery of nitrogen at a low temperature

TEMPERATURE IN MORNING	NITROGEN AS NITRATE IN SOIL ALONE	NITROGEN AS NITRATE ADDED TO SOIL	NITROGEN AS NITRATE RECOVERED	RECOVERY OF ADDED NITROGEN
°C.	p.p.m.	p.p.m.	p.p.m.	p.p.m.
14	2.63 } 2.58 2.52	25 25	27.22 } 27.48 27.74	24.90

TABLE 9

	AMOUNT OF NITRATE NITROGEN REDUCED	AMOUNT OF NITRATE NITROGEN PRESENT IN TRAP	MINIMUM LOSS IN TRAP	RECOVERY		AVERAGE PERCENTAGE RECOVERY
	mgm.	mgm.	per cent	mgm.	per cent	per cent
A	0.25	0.0115	4.6	.....	...	...
B	2.5	0.029	1.2	.....	...	...
C	0.25	.....	...	0.288	115	} 115
D	0.25	.....	...	0.288	115	
E	2.5	.....	...	2.40	96	} 99.6
F	2.5	.....	...	2.58	103.2	

by the hydrogen. We therefore substituted another form of trap. This consisted of a Soxhlet (sugar) tube with a narrow constriction, thrust through the hole of a rubber stopper fitted into the neck of the Erlenmeyer flask. The tube was packed with glass wool. When everything was ready for reduction and the stopper placed in position 0.1 N HCl (ammonia free) was poured over the glass wool. The constant evolution of hydrogen prevented the acid being sucked back beyond the constriction of the Soxhlet tube and any ammonia carried forward by the hydrogen was absorbed by the acid. This was all washed back into the flask before the solution was distilled.

Some investigation was done to determine the amount of ammonia which finds its way into the trap. Difficulty was experienced in removing the trap without allowing some of the acid to run back into the flask. But the results in any case show the minimum amount of ammonia collected by the trap.

Six separate determinations were done simultaneously, in four of which the liquid was washed back into the flask. Table 9 shows the results obtained.

Under these circumstances the determination can be considered quantitative. There is a tendency to get slightly high percentage when very small quantities of nitrate are reduced, but this is probably due to the concentration of the minute traces of ammonia in the water used for the determination.

After reduction the ammonia was distilled off into 10 cc. of 0.1 N HCl, and the distillate made up to a definite volume. Aliquots were then taken and Nesslerized. The experimental error introduced by comparing the tints produced with standard tints in Nessler tubes was found too large in view of the small quantities of nitrates the author was working on. Recourse was therefore had to the Schreiner Colorimeter. The only instrument available, after being slightly modified, was found to give very reliable results.

It was found inconvenient to move the eye laterally when viewing the colorimeter images and it also made accurate tint comparison unduly difficult. The mirror was therefore removed and cut in half vertically. The two halves were then placed at a slight angle so that both images could be viewed from the same point. This was found greatly to facilitate the comparison. When the work was first undertaken persistent increasing or decreasing ratios were obtained by the colorimeter, depending on the lengths of the columns. The following ratios taken at random, will serve as an example (1.03; 1.06; 1.06; 1.08; 1.13; 1.14; 1.18). This was found very annoying and the phenomenon was traced to the optical effect produced by the curvature of the inside bottom surfaces of both the outer and inner tubes of the colorimeter. The corresponding outer surfaces were optically plane. This irregularity in the glass was very much more pronounced in the small inner than the outer tubes; as was shown by the distortion produced in print when viewed through the tubes. It was remedied in the following manner: Water was poured into the inner tube. This minimized the lens effect at the bottom surface of contact, but the meniscus at the upper surface of the water now remained. A rubber ring was placed inside the top end of the tube, and sufficient water was poured in just to cover the upper edge of this ring. A microscope cover-glass was then placed so as to float by surface tension on the surface of the water, its upper surface remaining dry. Practically no distortion was now produced when print was viewed through the combination. In all subsequent work done with the modified colorimeter the ratios were found to be constant, and independent of the lengths of the columns of liquid.

In actual work with the colorimeter the following conditions were observed:

(1) The standard solution contained 0.03 mgm. of nitrogen in the form of ammonium chloride, and occupied a volume of 100 cc.

(2) All solutions to be compared had to be perfectly clear. A slight turbidity produced when the Nessler's solution contained any suspension interfered greatly with the accuracy.

(3) All solutions to be compared with the standard had to give ratios as close to 1 as possible.

(4) Solutions which had to be compared with each other had to be prepared at the same time.

(5) After mixing with Nessler's solution at least 20 minutes had to elapse before comparing tints since it was found that some ratios became constant only after that interval of time, especially if they deviated to any extent from 1.

After some practice with the method with all the improvements described above, it was possible to obtain very satisfactory results. The last set of eight determinations of nitrate gave the results shown in table 10. They represent four duplicate experiments.

The last column of figures is given in order to give an idea of the error involved if titration were resorted to instead of the Nesslerization. The average difference is equivalent to less than 0.02 cc. of 0.02 N acid.

TABLE 10

Nitrate nitrogen in dry soil

EXPERIMENT NUMBER	NITROGEN DETERMINED	AVERAGE OF DUPLICATES	DIFFERENCE BETWEEN DUPLICATES		DIFFERENCE IN NESSLERIZATION BETWEEN DUPLICATES	DIFFERENCE BETWEEN DUPLICATES CALCULATED TO 50 GM. SOIL
	p.p.m.	*p.p.m.*	*p.p.m.*	*per cent*	*mgm. of N*	*mgm.*
A	1.29 1.21	1.25	0.08	6.4	0.00165	0.0044
B	1.38 1.21	1.3	0.17	13.1	0.0021	0.0056
C	3.0 3.0	3.0	0	0	0	0
D	1.9 1.78	1.84	0.12	6.5	0.0024	0.006
Average	1.848	1.848	0.093	6.5	0.00154	0.004

TABLE 11

Summary of ninety-two nitrate determinations

	AVERAGE NITRIC NITROGEN	AVERAGE DIFFERENCE BETWEEN DUPLICATES		GREATEST DIFFERENCE BETWEEN DUPLICATES
	p p.m.	*p.p.m.*	*per cent*	*p.p.m.*
First set: (0.94–4.51 p.p.m.)	1.892	0.111	5.87	0.27
Second set: (6.44–13.58 p.p.m.)	8.736	0.319	3.65	0.90

Taking the last 92 nitrate determinations done by the author consisting of 46 duplicate sets and omitting no results obtained, table 11 can be constructed. The reliability of the method can then be guaged from a consideration of the differences between duplicates. The results are arranged in two sets, the first set consisting of 62 individual determinations where the nitrate nitrogen ranges from 0.94 to 4.51 parts per million of oven-dried soil. The second set contains 30 separate determinations in which the range is from 6.44 to 13.58 parts per million.

No account was taken of "blanks" in the above work. A number of blank determinations were done, starting from different points in the process, as

well as for the complete process. In all cases the amount of nitrate found in a
blank was extremely small, and seemed to vary more with different batches of
ammonia-free water than with any other factor. It was also found that by
far the greatest portion of this amount was produced during the last stage of
the work, namely, the distillation of the reduced solution. A small amount
of ammonia persistently adhered to the rubber connections of the distillation
apparatus and could only be removed very slowly by the repeated boiling of
ammonia-free water in the apparatus. This cannot, strictly speaking, be
considered a "blank" since it is more of the nature of a "constant." Whatever
ammonia is given off by the apparatus in any particular determination is
replenished again from the ammonia distilling over. Care should however
be taken, if great accuracy is desired, that soils with very divergent quantities
of nitrate be not worked on at the same time (if aliquots representing the
same amount of soil are taken for reduction) since the above "constant" may
then vary. The true blank might then become appreciable. For the sake of
completeness it may be stated that the blanks varied from 0.0040 to 0.013 mgm.
of nitrogen per 100 cc. of distillate. Since less than 100 cc. of the distillate
is generally taken for Nesslerization, we see that the effect of the blank may
be considered negligible.

<div style="text-align:center">DESCRIPTION OF METHOD ADOPTED</div>

The complete process for the determination of the nitrate in any soil may
now be described in detail.

One-hundred grams of the oven-dried soil sample are placed in a shaking bottle,
200 cc. of distilled water, free from nitrates, is added, 0.5 cc. of chloroform is
poured in, and the bottle closed. The bottle with its contents is shaken
in a rotary shaker for 90 minutes. (This time factor has not yet been studied
and much less time may suffice.) Four grams of CaO are introduced into the
bottle and the shaking continued for another 30 minutes. The contents are
then poured into a ribbed filter and filtration continued until a suitable amount
of filtrate is obtained. This generally takes from $\frac{1}{2}$ hour to $2\frac{1}{2}$ hours with heavy
soils. With some very clayey soils it is sometimes advantageous to filter from
two funnels. An aliquot portion of the filtrate is then poured into a porcelain
evaporating dish and 15 cc. of a 10-per cent solution of NaOH added. The
mixture is boiled down to about one-third of the original volume in order to
drive off any ammonia present. After cooling, the contents are washed over
into a 300 cc. wide-mouthed Erlenmeyer flask with ammonia-free water.
This flask has a mark made on its outside indicating the level of liquid
when it holds 150 cc. It also contains three large curls of aluminum foil
made from three strips each 15 cm. long by $\frac{1}{2}$ cm. wide, the three together
weighing about 1.5 gm. The curls should be arranged so as to occupy uni-
formly the space to be filled by the liquid. The flask is filled with water up
to the 150 cc. mark after the nitrate solution has been transferred. A trap
is then inserted into the mouth of the flask consisting of a rubber stopper

holding a Soxhlet (sugar) tube with a narrow constriction. The Soxhlet tube is packed with glass wool over which 0.1 N HCl is poured. This is generally done late in the afternoon, and the flask and its contents are left until the following morning, at room temperature. Reduction should then be complete. Where the night temperatures are very low (say below 15°C.) it would be advisable to use an incubator, and keep the temperature of reduction about 20°C. After 17–19 hours reduction the liquid in the trap is washed down into the reduction flask with ammonia-free water, and the liquid contents of the latter in turn washed into a 500 cc. distillation flask; 10 cc. of 10-per cent NaOH are added. The flask also contains a few pieces of granulated zinc in order to prevent bumping. After connecting to the condenser, the liquid, which should occupy about 250 cc. is brought to boiling and the distillate collected in 10 cc. 0.1 N HCl. The distillation is continued until the distillate and washings will almost fill a 200 cc. flask to the mark. After making up to the mark and shaking, suitable aliquots are taken for Nesslerization. The amount to be taken is found by trial, since it is necessary in an accurate determination that the colors given by the aliquot and the standard be very nearly the same. The Schreiner colorimeter with certain modifications is very suitable for comparing the tints. One cubic centimeter of the standard NH_4Cl solution containing 0.03 mgm. nitrogen is diluted to 100 cc. in the colorimeter tube. The aliquots are treated similarly. When all the solutions (if there is more than one nitrate determination) are made up to 100 cc. and mixed, 2 cc. of Nessler's solution are added to each. After shaking, at least 20 minutes should elapse before comparing the tints.

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THE CALCIUM CONTENT OF SOIL IN RELATION TO ABSOLUTE REACTION[1]

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INTRODUCTION

The importance of reaction in soil investigations is emphasized by the long lists of references given by Fisher (3) and McIntire (10) as well as others. The cause and nature of soil acidity have received a great deal of study (5, 6, 16). Recent developments in physical chemistry have served to clarify the terms acid, neutral, and alkaline. In an acid solution the hydrogen ions are in excess, in an alkaline solution the hydroxyl ions are in excess, while in an absolutely neutral solution the concentrations of these two ions are equal. Since water contains both these ions it follows that a water suspension or a water extract of soil always contains both hydrogen ions and hydroxyl ions and acidity or alkalinity is determined by the one in excess. The more nearly equal the concentrations of these two ions, the more nearly neutral is the soil reaction. This is the meaning of soil acidity as used in this discussion; however, it is recognized that the term may have a much wider application (9).

The fundamental cause of an acid condition of soil is the removal of bases by the process of weathering. A suspension of finely ground orthoclase in water gives an alkaline reaction which may be written:

$$KAlSi_3O_8 + HOH = KOH + KAlSi_3O_8$$
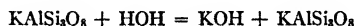
Qualitatively, the same reaction would take place regardless of the base present in the original mineral. Under humid climatic conditions the bases are converted into carbonates, in which form they are leached away and the acid-alumino-silicates accumulate in the soil. The reaction is not as simple as indicated by this equation but it serves to illustrate the process. Organic matter is an indirect cause of soil acidity in that its decay promotes the decomposition of those minerals which go to make up the soil.

Under present climatic conditions calcium is leached from the surface soil much more rapidly than many other bases (7). That certain bases are not leached from the soil as rapidly as others is illustrated by the following example (14). In twenty-six Kansas soils formed from limestone, the average content of calcium in the surface soil was found to be 0.75 per cent and that of potassium, 1.80 per cent. The average content of calcium in three hundred forty-five limestones was found by Clarke (2) to be 30.45 per cent and that of potassium 0.27 per cent. The average content of potassium in Kansas soils is about three times as great as that of calcium (14, 15). Potassium is evidently held more firmly by the alumino-silicates than calcium. When a neutral salt like potassium chloride is added to a soil containing alumino-silicates, the potassium is strongly absorbed (11) and bases like calcium are set free (17), and thus lost by leaching. Lyon and Bizzel (8) have reported a loss of

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calcium equivalent to 730 pounds of calcium carbonate from the unlimed and seven hundred forty-three from the limed soil during one year.

From the foregoing discussion it would seem that the calcium content of the soil might bear some relation to soil reaction and since it has been well established that soil reaction is a dominant factor in the growth of many forms of plant life it was thought worth while to study the relation between the calcium content of soil and the absolute reaction. The soils used by Gainey (4) in investigating the relationship between soil reaction and Azotobacter were available and since the absolute reaction as well as their Azotobacter content were already known they were used in this study.[2]

METHODS

Since it has been established that the calcium soluble in normal hydrochloric acid bears a closer relation to reaction than the total calcium (15), it was decided to determine calcium by the following method:

Twenty-five grams of soil were placed in 500-cc. wide-mouth, rubber-stoppered bottles and 250 cc. normal HCl added, after which the bottles were shaken on a shaking machine for several hours. After settling, aliquot portions were removed with a pipette and the calcium determined in the usual way. Preliminary trials indicated that filtering and washing the acid insoluble residue did not add to the accuracy.

For convenience in study, the results obtained are divided into three groups. Group 1 includes all soils taken in the vicinity of Manhattan, Riley County, Kansas; group 2, all soils from other counties in Kansas; group 3, all soils obtained from experiment stations in other states. The figures for the hydrogen-ion concentration (electrometric), as well as the symbols + and − indicating presence or absence of Azotobacter, are the same as those reported by Gainey (4).

SOILS FROM RILEY COUNTY

For the soils in group 1, the type was known and in studying the results it soon became evident that soil type was one of the factors to be considered in correlating the amount of calcium with the absolute reaction. As the number of soils for each type was small, it was thought best to class the soils by series. The results obtained on soils in group 1 are found in table 1.

The figures under each of the soil series are arranged according to increasing numerical values of pH. It is at once apparent that there is a general correlation between the pH values and the percentages of calcium; in a general way as the percent of calcium increases, the alkalinity also increases, however, there are some exceptions.

[2] Not all of the soils used in the former study were included, partly because some were duplicates and partly because in some instances sufficient amount of soil was not available for the chemical determination.

TABLE 1

Relation between absolute reaction, calcium soluble in normal hydrochloric acid, and Azotobacter content of soils of group 1, Riley county, Kansas

SOIL NO.	AZOTO-BACTER	pH VALUES	PER-CENT-AGE OF Ca	SOIL NO.	AZOTO-BACTER	pH VALUES	PER-CENT-AGE OF Ca	SOIL NO.	AZOTO-BACTER	pH VALUES	PER-CENT-AGE OF Ca
Marshall clay loam				*Wabash silt loam—Cont.*				*Summit silt loam (colluvial)— Cont.*			
49	—	5.03	0.17	38*	+	5.59	0.31	64	+	6.35	0.35
21	—	5.05	0.20	71	+	5.61	0.40	40	+	6.72	0.42
23	—	5.10	0.18	28*	+	5.81	0.19	34	+	6.74	0.30
22	—	5.27	0.20	27*	+	5.88	0.33	56‖	+	7.18	0.33
				39*	+	6.05	0.34	63**	+	7.43	0.55
Marshall silt loam				25†	+	6.45	0.44	59	+	7.49	0.80
69	—	5.19	0.20	42	+	7.05	0.39	55‖	+	7.50	0.44
50	—	5.32	0.19					87††	+	7.59	4.45
66	—	5.81	0.29	*Osage silt loam*				83	+	7.72	5.59
65	—	5.94	0.21	77	—	5.34	0.24				
41	+	5.98	0.29	76	—	5.63	0.26	*Laurel fine sandy loam*			
70	+	6.93	0.33	73	—	5.88	0.44	46	—	6.03	0.15
29*	+	7.27	0.56	88	+	6.88	0.41	84	+	7.47	1.38
				90	+	7.06	0.54	82	+	7.60	7.92
Oswego silt loam				74	+	7.25	0.61	81	+	7.77	0.74
24	—	4.90	0.24	75	+	7.30	0.63	31‡‡	+	7.71	0.93
60	—	5.73	0.30	86	+	7.60	0.43				
68	+	6.05	0.25	85‡	+	7.62	1.11	*Laurel very fine sandy loam*			
57	+	7.30	0.50	89‡	+	7.76	0.97	48	+	6.52	0.22
								45	+	7.45	0.53
Wabash silt loam				*Summit silt loam (colluvial)*				47	+	7.52	0.68
				58§	—	5.46	0.17	44	+	7.71	0.46
67	—	5.32	0.32	32	—	5.85	0.26	80	+	7.84	0.90
61*	—	5.51	0.29	54	+	6.18	0.27	79‖‖	+	8.48	0.38

* Silty clay loam.
† Silty clay.
‡ Fine sandy loam.
§ Stony loam.
‖ Loam (colluvial).

** Silt (colluvial).
†† Stony loam (creek bank).
‡‡ Silt loam.
‖‖ Medium sand.

The coefficients of correlation between pH numbers and percentages of calcium were calculated by the usual formula for each soil series except the Laurel. The results obtained were:

Marshall series... 0 899 ± 0.0389
Oswego series... 0.912 ± 0.0663
Wabash series... 1.000 ± 1.1135
Osage series... 0.805 ± 0.0338
Summit series.. 0.557 ± 0.1290

This correlation is good except for the Summit series. The figures in table 1 show that the last two soils of this series had about ten times as much calcium as the average of the others in the series, while the increase in pH was comparatively very small. When calcium is present in the form of a carbonate the amount, beyond a certain limit, has very little influence on the pH. The coefficient of correlation was recalculated for the Summit series leaving out the last two soils. The coefficient of correlation thus obtained was 0.781 ± 0.0675. The lack of correlation in the Laurel series is probably due to the presence of calcium in the form of carbonate even when only small amounts are found, and also the influence of sand.

SOILS FROM OTHER COUNTIES OF KANSAS

The type of soil of those samples obtained from different counties in Kansas was not known, only a very general description being available. Meager as this information was it helps to explain the results in some cases. In studying the pH values and percentages of calcium it soon became evident that the results from the eastern part of the state could not be compared directly with those from the western part of the state, due probably to the more frequent occurrence of carbonate in the soils of the western part, even when the content of calcium was comparatively small. For this reason the data were arranged separately for each county according to the increase in pH values; also the data from the counties in the eastern and central parts of the state were placed in one sub-group, and the data from the counties in the extreme western part of the state were placed in another sub-group.

The data as arranged are given in tables 2 and 3. In each sub-group the counties are arranged in alphabetical order.

In using the hydrogen electrode on soils the analytical error is probably about 10 millivolts. This means that differences of 0.15 pH or possibly 0.2 pH are not significant. This is a large figure when compared with results obtained with the hydrogen electrode on pure solutions. Several investigators have found that it is practically impossible to obtain very close duplicates on pH values on soils. The reasons for this do not seem to be known. The analytical error in the calcium determination can be considered about one milligram.

If the data presented in tables 2 and 3 are studied with regard to these considerations, it will be found that within each county there is a close relation between the pH numbers and the percents of calcium; the higher the calcium the higher the pH number. This statement holds true for all the counties and all the soils with the following exceptions:

The difference in calcium content of soils 176 and 177, Anderson County, is not significant while the difference in pH is large. This is explained by the fact that soil 176 was sandy while 177 was a silt soil. The same explanation probably holds true for soil 166 from Cloud County and 175 from Franklin County. Soil 240 from Pawnee County, with the highest pH value and

TABLE 2

Relation between absolute reaction, calcium soluble in normal hydrochloric acid, and Azotobacter content of soils in counties of eastern and central Kansas

SOIL NO.	AZOTO-BACTER	pH VALUES	PERCENT-AGE OF Ca	SOIL NO.	AZOTO-BACTER	pH VALUES	PERCENT-AGE OF Ca	SOIL NO.	AZOTO-BACTER	pH VALUES	PERCENT-AGE OF Ca
		Anderson				*Elk*				*Morris*	
178	−	5.30	0.20	242	−	5.90	0.25	238	−	5.54	0.25
177	−	5.37	0.30			*Franklin*					
176	+	6.35	0.31							*Nemaha*	
		Atchison		169	+	5.10	0.23				
				168	−	5.17	0.32	180	−	5.47	0.37
191	−	5.32	0.30	175	−	5.29	0.23	179	−	5.76	0.36
190	−	5.34	0.28	174	−	5.85	0.32				
189	−	5.52	0.33			*Greenwood*				*Osborne*	
188	+	5.52	0.37								
				254	−	4.68	0.25	201	−	5.98	0.29
		Bourbon		210	−	5.05	0.16	230	+	6.98	0.47
				211	−	5.10	0.23	200	+	8.28	1.12
229	+	7.60	0.72	217	+	5.15	0.27				
				212	−	5.39	0.23			*Pottawatomie*	
		Chase		209	−	5.53	0.33				
196	−	4.90	0.31	233	+	7.47	0.54	220	+	6.34	0.30
195	−	5.69	0.29								
197	+	7.57	0.43			*Jackson*				*Pratt*	
		Chautauqua		277	−	5.10	0.17				
				276	−	5.27	0.20	261	−	5.81	0.23
237	−	5.02	0.21					273	−	6.42	0.16
244	−	5.22	0.44			*Jewell*		262	−	7.23	0.32
236	−	5.30	0.34								
				194	+	6.15	0.28			*Washington*	
		Cloud		193	+	6.84	0.41				
				219	−	7.25	0.46	204	−	5.10	0.17
164	−	5.41	0.16	218	+	7.28	0.33				
165	−	5.54	0.18			*Lyon*				*Wilson*	
166	−	5.71	0.17								
163	+	5.98	0.30	263	−	4.93	0.30	172	−	5.02	0.16
				198	−	5.49	0.36	171	+	5.15	0.18
		Coffey		199	+	6.07	0.53	192	−	5.22	0.26
								170	+	5.93	0.33
252	−	5.37	0.29			*Marshall*					
251	−	6.10	0.39							*Woodson*	
				181	+	6.10	0.24				
		Doniphan		182	−	6.52	0.32	271	−	5.41	0.16
206	−	5.32	0.19	184	+	6.77	0.39				
205	+	6.02	0.22	183	+	7.37	0.59				
207	+	7.94	0.84							*Wyandotte*	
		Douglas				*McPherson*					
								185	−	5.44	0.22
249	−	5.12	0.22	228	−	5.20	0.21	167	+	6.25	0.27
247	−	5.37	0.28	227	−	5.66	0.26	187	+	6.69	0.38
248	−	5.47	0.24	225	+	5.91	0.33	186	+	7.72	0.54
246	−	5.90	0.25	226	+	7.13	0.38				

lowest calcium content, was a sand from a sand dune.   Soil 195, Chase County, has less calcium than soil 196 although it has a larger pH number.   No explanation is available. ˙This same statement applies to soil 244, Chautaqua County; soil 210 from Greenwood County; soil 243 Meade County; soil 179, Nemaha County; soil 273, Pratt County; and soil 214, Rawlins County. The high pH value of soil 218 from Jewell County, the calcium content of which is less than that of soils with lower pH values is probably due to the fact that soil 218 was from a second creek bottom and the calcium was possibly present in a more soluble form.

TABLE 3

Relation between absolute reaction, calcium soluble in normal hydrochloric acid, and Azotobacter content of soils in counties of western Kansas

SOIL NO.	AZOTO-BACTER	pH VALUES	PER-CENT-AGE OF Ca	SOIL NO.	AZOTO-BACTER	pH VALUES	PER-CENT-AGE OF Ca	SOIL NO.	AZOTO-BACTER	pH VALUES	PER-CENT-AGE OF Ca
Finney				*Logan*				*Rawlins*			
274	+	6.96	0.19	259	+	6.49	0.34	215	+	7.28	0.36
275	+	8.06	1.26					216	+	7.40	0.30
Ford				*Meade*				214	+	7.98	0.82
				241	+	6.18	0.27	213	+	8.30	0.66
223	+	6.63	0.32	235	+	6.66	0.38	*Rush*			
221	+	6.66	0.28	243	−	6.96	0.21				
222	+	6.69	0.25	234	+	8.15	1.01	208	+	7.60	0.57
224	+	7.52	0.35	*Pawnee*				*Thomas*			
Hodgeman				239	+	6.08	0.21	260	−	7.48	0.40
230	+	6.51	0.37	173	+	6.08	0.23	*Wichita*			
264	+	7.52	0.64	253	+	6.25	0.57				
278	+	7.99	1.04	240	+	7.03	0.12	256	−	6.35	0.30
Kearney								255	+	7.79	0.45
203	+	7.25	0.35								
202	+	8.19	0.56								
231	+	8.25	0.65								

These exceptions are few when the total number of soils involved are considered, and it shows that as a rule the higher the calcium content the higher the pH value.   A smaller amount of calcium, however, is more effective in raising the pH value in a sandy soil than in a clay or silt soil.   The calcium may be in a condition of greater solubility in a sandy soil, or a larger amount of calcium is required to balance the acid properties of the alumino-silicates in a clay or silt soil.

The pH value on soils from the drier portion of the state is higher for the same range of calcium than on the soils from the more humid sections.   In

the eastern part of the state calcium is not present in the form of carbonate unless the amount is large.   In the western part calcium may be present in the form of carbonate even though the amount present is very small.   This means that climate as well as soil type is a factor which must be considered in correlating the calcium content of the soil with the pH value.   The coefficient of correlation between the pH value and the calcium content was found to be 0.747 ± 0.013 for the soils from the more humid part of the state and 0.745 ± 0.0372 for the soils from the drier part of the state.   This is a good correlation when the variations in the range of soil types are considered.

SOILS FROM OTHER STATES

The data obtained on soils from other experiment stations are presented in tables 4, 5 and 6.   In table 4 are grouped those soils which are from the non-glaciated area, and in table 5 those from the glaciated area of central and eastern states.   In table 6 are presented the data obtained on the soils from California and Oregon.   A number of the soils here reported are known to have been limed more or less recently.   The quantity of lime added as well as the period elapsing since lime was applied are undoubtedly factors of importance in determining the influence of such treatment upon the absolute reaction.

These soils represent a variety of climatic conditions.   As a rule the soils from the eastern and southeastern states have a much lower calcium content than the soils from the central states.   With a few exceptions the soils from the limed plots have a higher calcium content than those from the unlimed plots in the same state.   As a general rule the high pH values are found in the soils having the higher calcium content when comparisons are made with soils from the same state.   The following soils are exceptions to this general rule; 306, California; 360, Georgia; 357, Illinois; 359, Indiana; 327, Iowa; 318, North Carolina; 323, 322, and 321, New Jersey; 303, Michigan; and 339, Oregon.   Two soils gave notably high pH values considering the low calcium content.   These are soil 324 from Iowa and soil 303, from Michigan. Both these soils were classed as sandy.   There are a few other minor exceptions but they fall within the limits of the analytical error.

Most of the soils presented in tble 4 have a calcium content of less than 0.15 per cent and a pH value less than 6.00.   On the other hand, most of the soils presented in table 5 have a calcium content of more than 0.15 per cent and pH values above 6.00.

The coefficient of correlation between the pH values and the percentages of calcium was found to be as follows:

Eastern and southern soils................................. 0.4625 ± 0.0054
Central and eastern soils............................. ...... 0.714 ± 0.0069
Western soils... 0.317 ± 0.1060

TABLE 4

Relation between absolute reaction, calcium soluble in normal hydrochloric acid, and Azotobacter content of soils in southeastern United States

SOIL NO.	LIMED	AZOTO-BACTER	pH VALUES	PERCENTAGE OF Ca	SOIL NO.	LIMED	AZOTO-BACTER	pH VALUES	PERCENTAGE OF Ca
Alabama					*North Carolina—Cont.*				
342	0	—	4.44	0.036	377	0	—	4.98	0.120
344	0	—	5.05	0.046	316	0	—	5.00	0.048
346	+	—	5.51	0.054	318	+	—	6.01	0.048
345	+	—	5.66	0.078	416	+	—	6.07	0.120
343	0	—	5.83	0.064	317	+	—	6.78	0.110
Arkansas					*Rhode Island**				
335	0	—	5.05	0.100	400	+	—	4.31	0.040
336	0	—	5.58	0.076	397	0	—	5.30	0.060
334	0	+	6.96	0.086	396	+	—	5.64	0.090
Georgia					399	0	—	5.88	0.100
362	0	—	5.24	0.056	*South Carolina*				
361	+	—	6.05	0.700	441	0	—	4.90	0.050
360	+	—	6.69	0.280	438	0	+	4.98	0.050
Kentucky					442	+	—	5.15	0.050
411	0	—	4.82	0.060	443	+	—	5.34	0.050
407	0	—	4.82	0.090	440	+	+	7.84	0.180
409	0	—	5.19	0.090	439	0	+	8.14	0.270
408	+	—	6.12	0.150	*Tennessee*				
412	+	—	6.62	0.160	422	0	+	4.53	0.080
Maryland					420	0	—	4.59	0.080
392	0	—	4.48	0.050	418	0	+	4.68	0.080
393	0	—	4.51	0.070	421	+	+	5.42	0.130
389	0	—	4.70	0.070	423	+	+	5.68	0.120
394	+	—	6.18	0.120	419	+	+	5.69	0.150
391	+	—	6.77	0.160	*Virginia*				
Mississippi					404	0	—	4.70	0.080
348	0	—	4.21	0.058	405	0	—	4.75	0.100
347	0	+	6.17	0.270	401	+	+	6.15	0.140
349	0	+	6.76	0.470	402	+	+	7.03	0.200
North Carolina					403	+	+	7.30	0.690
379	0	—	3.73	0.032	*West Virginia*				
417	0	—	4.66	0.040	428	0	—	3.99	0.040
415	0	—	4.81	0.040	426	0	—	4.02	0.040
378	0	—	4.90	0.036	424	0	—	4.09	0.060
380	0	—	4.93	0.060	425	+	—	4.66	0.080
414	+	—	4.97	0.050	427	+	—	4.90	0.080
					429	+	—	5.51	0.090

* Classed with this group because of soil type.

TABLE 5

Relation between absolute reaction, calcium soluble in normal hydrochloric acid, and Azotobacter content of soils in eastern and central United States

SOIL NO.	LIMED	AZOTO-BACTER	pH VALUES	PERCENTAGE OF Ca	SOIL NO.	LIMED	AZOTO-BACTER	pH VALUES	PERCENTAGE OF Ca
		Illinois					*New York*		
355	0	—	4.19	0.069	436	0	—	4.98	0.120
356	0	—	4.70	0.220	333	0	—	5.47	0.120
353	0	—	5.00	0.190	435	+	—	6.23	0.190
357	+	—	5.73	0.460	332	+	—	6.23	0.210
354	+	+	6.51	0.240	437	+	+	6.72	0.190
352	+	+	7.20	0.400	433	+	—	6.78	0.190
					331	+	+	6.79	0.180
		Indiana			330	+	+	6.84	0.180
					434	+	+	6.84	0.190
430	0	—	4.58	0.070	329	+	+	7.20	0.240
359	+	—	4.93	0.270	432	+	+	7.30	0.250
431	+	+	5.03	0.150					
		Iowa					*Massachusetts*		
325	0	—	4.78	0.200	388	0	—	4.10	0.040
326	0	—	4.83	0.250	387	0	—	4.10	0.050
327	0	+	4.93	0.600	386	+	—	5.24	0.070
328	0	—	5.88	0.240	385	+	—	5.31	0.100
324	0	+	7.11	0.270	384	+	—	6.27	0.200
					383	+	—	6.29	0.170
		Michigan					*Ohio*		
305	0	—	5.69	0.220					
301	0	—	5.76	0.120	313	+	—	5.05	0.076
302	0	+	6.64	0.250	314	0	—	6.03	0.170
303	0	—	7.38	0.140	315	0	—	6.07	0.150
					367	+	—	6.18	0.150
		Missouri			366	+	+	6.84	0.250
					311	+	—	7.01	0.230
265	0	—	4.36	0.130	369	0	+	7.05	0.490
266	0	—	4.97	0.190	312	+	—	7.33	0.260
267	+	+	7.10	0.420	370	0	+	7.45	0.430
					368	0	+	7.48	0.390
		New Jersey							
371	0	—	4.70	0.099			*Pennsylvania*		
320	0	—	4.80	0.150					
323	0	—	4.90	0.260	449	0	—	4.24	0.040
372	+	—	5.37	0.140	446	0	—	5.07	0.110
374	+	—	6.44	0.160	445	0	—	5.59	0.130
321	+	—	6.52	0.290	444	0	+	7.20	0.360
319	+	—	6.71	0.240	448	+	+	8.25	1.210
322	+	—	6.93	0.160	447	+	+	8.41	1.200

Only one group shows good correlation. It was thought that liming might be the cause of this lack of correlation, accordingly, the coefficients of correlation of the unlimed soils were calculated and found to be as follows:

Eastern and southern soils................................... 0.381 + 0.0137
Central and eastern soils.................................... 0.525 + 0.0082

Evidently, liming is not the cause of the lack of correlation.

TABLE 6

Relation between absolute reaction, calcium soluble in normal hydrochloric acid, and Azotobacter content of soils of California and Oregon

SOIL NO.	LIMED	AZOTO-BACTER	pH VALUES	PERCENT-AGE OF Ca	SOIL NO.	LIMED	AZOTO-BACTER	pH VALUES	PERCENT-AGE OF Ca
		California					*Oregon*		
307	0	—	5.49	0.18	339	0	—	5.24	0.22
306	0	+	5.61	0.41	337	0	—	5.27	0.16
308	0	—	5.81	0.30	338	0	—	5.39	0.35
310	0	+	7.08	0.34	341	0	—	5.66	0.48
					340	0	—	5.93	0.62

SUMMARY AND CONCLUSION

A large number of soils obtained from the vicinity of Manhattan, Riley County, Kansas and also from various counties in the state and from different experiment stations of the United States were analyzed for calcium soluble in cold normal hydrochloric acid. The growth of Azotobacter and the pH values had been previously determined on these soils. There exists a close correlation between the calcium content and the pH value of soils of similar physical texture collected under similar climatic conditions.

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"AUXIMONES" AND THE GROWTH OF THE GREEN PLANT[1]

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The possibility of the presence in the soil of growth-promoting accessory substances is still an open question. The nutrition of the green plant has generally been regarded as satisfied by a supply of inorganic food materials, consisting of mineral matter, carbon dioxide and water, from which organic material is produced and the complete plant structure built up. Recently, however, this conception has been questioned by Bottomley (1–6) and Mockeridge (15) who have stated that the addition of minimal quantities of certain organic substances to the inorganic nutrients is absolutely essential if the plants are to grow healthily and normally for any length of time.

To these organic substances Bottomley gave the name *auximones*, and it was suggested that they were similar in function to the growth-promoting accessory factors termed vitamines, necessary for the growth of animals. "It is now established that plants, in their turn, require growth-promoting substances, or auximones; which, in the case of the lower plants, are apparently manufactured by themselves, but which in the case of green plants, must be supplied from without. Since these necessary accessory substances are essentially organic in nature, their only possible source in the case of ordinary green plants is to be found in the organic matter of the soil in which they are growing."

Several patents were secured by Bottomley for the manufacture of these growth-promoting substances from bacteria-treated peats, and an effort was made to use the *auximones* on a commercial scale in both greenhouse and market garden practise. A popular account is given by G. D. Knox in *The Spirit of the Soil* and marked success is reported in many cases.

In order to avoid introducing the *auximone* in the seed, Bottomley worked in the laboratory principally with *Lemna minor* and *Lemna major* which reproduce by budding, using Detmer-Moor's and Knop's solutions (6). With these solutions he failed to get good growth and after a few weeks both the appearance and weight of the *Lemna* indicated that the plants were not receiving all that they required to maintain their normal health. Mockeridge (15) had the same experience with *Lemna major*. In both cases the addition of small quantities of organic matter, extracted from soil or from the specially treated peat, greatly increased the rate of reproduction and the health of the plants.

Mockeridge has quoted the work of Williams (20) who arrived at the conclusion that a substance identical with the water-soluble vitamine B was necessary for the growth of yeast. The experience of one of the writers with *Saccharomyces cerevisiae* (7) and recent work in these laboratories by Fulmer (9) and Nelson (16) as well as reports by McCollum and his co-workers (13) have shown that the accessory substance for yeast, the *Bios* of Wildiers (19), is of the nature of an accelerator rather than an essential for reproduction and cannot be compared with animal vitamines without which reproduction and growth cannot take place. Robertson

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(17) has suggested that this may be the same *substance X* which he finds accelerates the reproduction of infusoria.

It seemed possible therefore, that the function of organic matter in the nutrition of green plants might be to increase the speed of reproduction and growth, rather than serve as an essential constituent, and that the reason for poor growth in Knop's and Detmer's solutions might be the unsuitability of the media used. Bottomley (6) recognized this when using Detmer's solution alone: he therefore tested Knop's and found that it checked his results with Detmer's, but he does not seem to have tried others. Mendiola (14) in a genetic study of *Lemna minor*, reported successful growth and even increased size of plants with a modified Pfeffer's medium which contained no organic matter.

EXPERIMENTAL

After preliminary experiments *Lemna major* was chosen and the three salts, monocalcium phosphate, potassium nitrate and magnesium sulfate, were used as a basis of the medium. These salts were first tested by Livingston and Tottingham (12) for wheat. Iron was added to the solutions as ferric phosphate and was made up as described in the Plan for Coöperative Research of the National Research Council (11); approximately 0.38 mgm. of $FePO_4$ were added to 250 cc. of the solutions.

The calcium and magnesium salts were made up in 0.05 M solutions at 20°C. and the potassium nitrate 0.20 M. A modified Shive's apparatus (18) was used for filling and the plants were grown in Pyrex beakers which were wrapped to the level of the liquid with paper, black inside and white outside, and covered with a watch glass to prevent the entrance of dust. Each beaker contained 250 cc. of solution and this was changed twice a week as with Bottomley and Mockeridge: no trouble was caused by algae or mold under these conditions. The beakers were weighed and water lost was replaced each morning; specially redistilled conductivity water was used in all cases— the laboratory distilled water had a decidedly toxic effect on the plants. The stock cultures were grown in soil solutions, 25 gm. of a Carrington loam soil to 200 cc. water, and renewed weekly. All cultures received direct sunshine in the afternoon only.

One hundred and twenty-five solutions were made up, being all combinations of the three salts in the following proportions:

$Ca(H_2PO_4)_2$	KNO_3	$MgSO_4$
moles per liter	*moles per liter*	*moles per liter*
0.0004	0.0016	0.004
0.001	0.004	0.001
0.002	0.008	0.002
0.003	0.012	0.003
0.004	0.016	0.004

Within a week all plants in solutions containing 0.002 mole of monocalcium phosphate had turned brown and were dying or dead. This was not due to excess of calcium or phosphate for when the ions were rearranged, greater amounts were not harmful. On the other hand, 0.008 mole of KH_2PO_4 per liter proved toxic in several combinations. The effect of hydrogen ions is being further studied.

At the end of two weeks, twenty-two cultures which showed the best development with regard to size, color and number were selected for tests on their rate of reproduction. All were healthy and varied little in size from the controls in soil solution—a condition still shown after four months growth in the mineral solutions. The ratio of calcium to magnesium varied from 2.5 to 0.25.

Given good conditions, the rate of increase at any time should be proportional to the number of plants present, whence

$$\log_{10} \frac{N}{N_o} = k \, (t - t_o)$$

If the logarithm of the number of plants is plotted on time, the result is a straight line with slope k. The variation in temperature and sunlight, and possibly the time of the growing season, would be expected to make the curve somewhat irregular, but remarkably uniform results were obtained. Two typical curves are shown in figures 1 and 2, solutions 435 and 486. At the points marked with the arrows the beakers became crowded and the number of plants was reduced to ten or twelve. As will be seen, this did not alter the slope of the curve. Figure 3 shows the soil control, which contained 25 gm. soil and 200 cc. water, changed twice a week as with the mineral solutions. The k for this is 0.058, indicating that a plant reproduced itself—the "generation time"—in 5 days, compared to $5\frac{1}{2}$ to $5\frac{3}{4}$ for the mineral solutions.

In figures 4 and 5 are plotted of Bottomley's curves for Detmer's solution alone and Detmer's plus peat extract (6). In both cases the plants started to reproduce during the first week at a rapid rate and a generation consisted of four to five days. This rate, however, was not kept up but fell to about twenty days for the mineral solution alone and to 11 days for the medium including the peat extract. Upon adding the extract the rate of reproduction was doubled but it did not approach that of the first seven days. Curves for Knop's solutions plotted from both Bottomley and Mockeridge show the same shape but the time is even longer.

No such drop is shown in figures 1 and 2, where the rate of growth continued at twice the speed shown after the first week in Bottomley's medium containing minerals and peat extract. The rate of reproduction shown in figure 1—after growing with sunshine during the afternoon only—was rather smaller than for the plants grown in Bottomley's greenhouse during the first
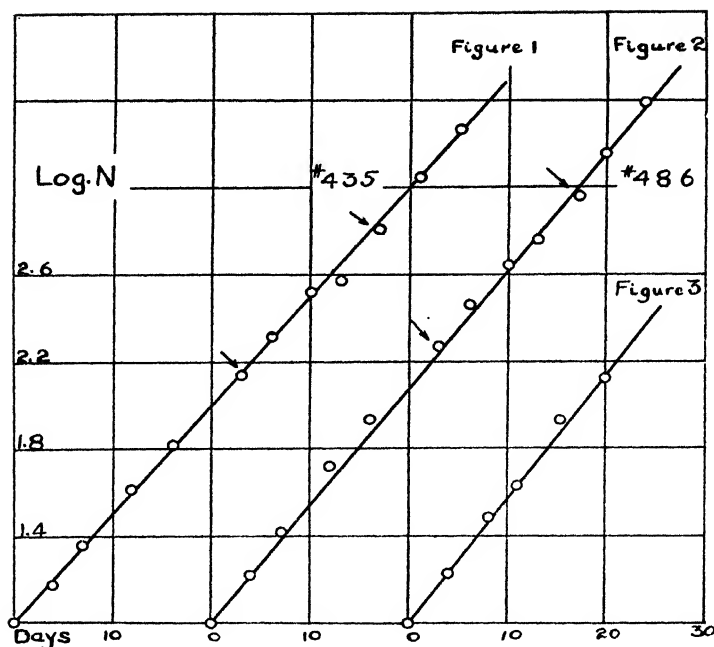
FIGS. 1–3. REPRODUCTION OF *Lemna* IN THREE SALT AND SOIL SOLUTIONS

FIG. 1. Solution no. 435. $Ca(H_2PO_4)_2 = 0.0004$ moles per liter; $KNO_3 = 0.0004$ moles per liter; $MgSO_4 = 0.0004$ moles per liter. $k = 0.051$. Generation time = 5.9 days.

FIG. 2. Solution no. 486. $Ca(H_2PO_4)_2 = 0.001$ moles per liter; $KNO_3 = 0.004$ moles per liter; $MgSO_4 = 0.002$ moles per liter. $k = 0.053$. Generation time = 5.6 days.

FIG. 3. Soil 25 gm.; water 200 cc. $k = 0.057$. Generation time = 5.2 days.
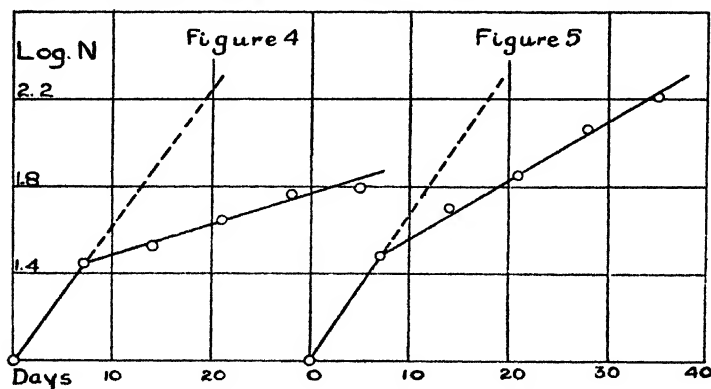
FIGS. 4–5. REPRODUCTION OF *Lemna* in DETMER'S SOLUTION

FIG. 4. Detmer's solution plotted from Bottomley's tables. Generation time for first week = 4.7 days; after first week = 20 days.

FIG. 5. Detmer's solution plus peat extract, plotted from Bottomley's tables. Generation time for first week = 4.3 days; after first week = 11 days.

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week in the peat solution, but this rate was almost maintained in the mineral solutions, whereas Bottomley's, even with organic matter present, dropped off rapidly.

It seems therefore, that better growth can be obtained by using a mineral solution suited to the plant than by adding organic matter to one in which the plant has difficulty in developing. For four months, representing over twenty generations, the *Lemna* without *auximones* reproduced at the same rate and the size and health of the plants showed no falling off. The suggestion that *auximones* act as essential constituents for growth of plants, in the same way as the vitamines for animals, must therefore be negatived. The question whether organic matter will function as an accelerator when the solution is adapted for the plant's needs is receiving further study in this laboratory.

SUMMARY

1. The growth of *Lemna major* in mineral solutions depends upon suitable concentrations of salts; organic matter is not necessary.

2. Reproduction, in varying concentrations of $Ca(H_2PO_4)_2$, KNO_3 and $MgSO_4$, with iron supplied as ferric phosphate, attained almost the speed for plants grown in solutions containing soil, and for four months the *Lemna* showed no signs of decrease in size.

3. The number of plants present follow closely the logarithmic equation $\log_{10} \frac{N}{N_0} = k(t - t_0)$. The time for one generation to produce another under the conditions given, for solutions containing soil was five days; for a number of different concentrations of the salts used a generation time of under six days was obtained.

4. *Auximones* are not essential for the growth and reproduction of green plants and cannot be classed with vitamines which are necessary for animal growth.

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THE EFFECT OF DIFFERENT KINDS OF WOOD AND OF WOOD PULP CELLULOSE ON PLANT GROWTH[1]

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In Wisconsin there are large tracts of land which at one time were covered with forest but which are now cleared of timber. Much of the eight million acres of cut-over land in Wisconsin is suitable for tillage and at present attempts are being made to cultivate these soils. Colby silt loam, the prevailing soil type, is decidedly acid and requires three to four tons of limestone per acre to neutralize the soil acids. With the use of mammoth tractors and disc plows, it is possible to turn over the soils including all the brush and vegetable growth which has sprung up since the removal of the timber. The material turned under often includes young trees one to four inches in diameter and the usual forest débris of leaves, roots, and brush.

For the first year after cultivation, the crop yield has usually been unsatisfactory, due no doubt to several causes. In this paper are recorded some results obtained from a laboratory and greenhouse study of the effect of different kinds of wood on the growth of oats and clover on these cut-over soils.

It is evident that the bad physical condition of the soil, resulting from the presence of this organic matter, would in a certain measure be responsible for the crop depression. It was soon recognized that the elimination of this factor does not remedy the matter but that the wood still exerts a depressing effect. The other factors may be of a biological nature. It is possible that such wood constituents as essential oil, resins, and tannins, may exert a toxic action on the plants or that abnormal conditions may be set up by these wood constituents or their decomposition products. The latter would probably be tied up with the formation and accumulation of nitrates. Nitrification may be inhibited, the nitrates may be reduced, or the nitrates may be assimilated (1) by the organisms decomposing such wood constituents as tannins, resins, etc., (2) by the organisms decomposing the cellulose in the wood, and (3) by those destroying the decomposition products of the cellulose.

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Only a few reports that deal directly with this subject have been found. Gibbs and and Werkman (4) investigated the effect of sawdust from various kinds of wood on ammonification and nitrification. They noted that the rate of nitrification of blood meal was slow and that there was an accumulation of ammonia. The nitrification of ammonium sulfate was depressed to a large degree. These investigators believed the depression is not due to a reduction of the nitrate but to an inhibition of the nitrate-forming organisms. Koch (6) found an entire absence of nitrate in soil containing 0.33 per cent cellulose as filter paper. In this soil he grew plants which attained the following dry weights:

	without paper	with paper
Buckwheat	22.0 gm.	3.0 gm.
Mangels	17.7 gm.	1.1 gm.

Eighteen months after treatment all the paper had disappeared and the soil began to show nitrate formation. He was able to demonstrate a considerable gain in total nitrogen in soil containing 3.0 per cent cellulose, some glucose, and which had been inoculated with azotobacter. In the first experiment, he did not estimate the total nitrogen and in the second he failed to measure the nitrates. In another paper, Koch (7) found that turpentine, resins, and tannins were toxic to plant growth and prevented nitrate accumulation. He suggests that these substances may be sources of energy for the denitrifying bacteria. In a later report (8) he found the same results but thought that the tannins might have had a toxic effect on the nitrate organisms.

Various other workers have reported on the nitrate content of forest soils: Baumann (1), and Henry (5) found that such soils are low in nitrate and that their power to form nitrates is low. Henry (5) also found that some forest soils gained in total nitrogen. Moriya (9) found that forest soils were high in nitrogen. Falckenstein (3) found that forest soils not lacking in lime could gain in nitrate.

EXPERIMENTAL WORK

In these experiments a virgin Colby silt loam, obtained from the timber area, was used. The dry soil contained the following percentages of nitrogen, phosphorus and potassium:

Nitrogen	0.088
Phosphorus	0.030
Phosphorus (available)	trace
Potassium	1.800

In order to make the tests somewhat similar to field conditions, the young trees or brush from the plot where the soil was taken were also saved and used in the experiments. It was found that the average weight of the green brush from an area of 10 square feet was 75 lbs. This consists of birch, willow, poplar and alder.

After a thorough mixing, the soil was filled into 4-gallon jars and the various woods added. The amount of wood to use was estimated from the weight of the brush on a known area. The first treatment, 1.5 per cent green weight, is approximately the same amount as turned under in the field; the second, 3.0 per cent green weight is more than is commonly applied. Aside from a comparison of the effect of the different woods, it was planned to try out the influence of size of wood particles and also the effect of ash from the various woods.

Two crops were sown, oats and red clover; the latter being subdivided into two sections, inoculated and uninoculated.

After the different applications of wood had been made, the soil moisture was brought up to 20 per cent. The soil was kept in this condition for sixty days and then planted. One-half of the jars, in duplicate, were planted to Swedish Select oats and the other half to red clover. For the plan and general treatment see the figures of tables 1 and 2.

TABLE 1

The effect of different kinds of wood on the growth of oats

NUMBER	TREATMENT	WEIGHT OF DRIED OAT PLANTS			
		Birch	Willow	Alder	Poplar
		gm.	*gm.*	*gm.*	*gm.*
1	None, control...........................	26.6	26.6	26.6	26.6
2	1.5 per cent wood coarse*................	19	19	17	18
3	3.0 per cent wood coarse*................	15	15	15	14
4	3.0 per cent wood fine*..................	28	24	15	17
5	3.0 per cent wood burned and ash used.....	26	29	29	26

* Green.

TABLE 2

The effect of different kinds of wood on the growth of red clover

NUMBER	TREATMENT	WEIGHT OF GREEN CLOVER PLANTS							
		Birch		Willow		Alder		Poplar	
		Not inoculated	Inoculated	Not inoculated	Inoculated	Not inoculated	Inoculated	Not inoculated	Inoculated
		gm.	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*
1	None, control........................	27.5	44	27.5	44	27.5	44	27.5	44
2	1.5 per cent wood coarse*..............	21	23	34	43	24	43	27	40
3	3.0 per cent wood coarse*..............	22	38	30	45	17	50	17	39
4	3.0 per cent wood fine*................	21	33	30	33	14	44	33	56
5	3.0 per cent wood burned and ash used...	54	54	67	60	56	58	63	52

* Green.

Almost without exception, the turning under of wood proved harmful to the growth of oats and in some cases to a very marked degree. This injury is far more noticeable in the case of alder and poplar than with birch and willow. Apparently the readily available part of the birch and of the willow was decomposed before the oats were planted. As might be expected, the decreased yield is greatest with the large application of wood. On the other hand the ash from the various woods failed to show any injury and frequently brought about a gain in growth of the oats and a very noticeable gain in the growth of the clover.

Plates 1, 2, and 3 show very clearly the effect of the different woods on the growth of oats. Without exception the plants in the jars containing the wood were a yellowish green color instead of the dark green noted in the control. From general appearances, these plants in the jars treated with wood suffered from lack of available nitrogen. Additional support for this statement is found in the results of the nitrate analysis. No nitrate nitrogen was found in the soil of the jars treated with wood while the controls showed small amounts.

The effect of the different woods on red clover is shown in table 2. In the main these results agree with those obtained from the oat experiment.

One point of special interest in the table is the decided improvement in growth of the inoculated red clover as compared with the uninoculated.

Where ashes are applied, this sharply defined influence of inoculation is not noted. To see if this good growth of the clover in the ash-treated soil is a result of plant food or of natural inoculation rendered effective by the food constituents of the ash, the roots of the inoculated and uninoculated plants in the ash-treated group were carefully examined for nodules. All of the inoculated plants showed nodules while all of the uninoculated plants were free of nodules. The evidence seems conclusive—nodule bacteria of red clover are not present in this soil, or if present, only in small numbers.

NATURE OF THE INJURIOUS FACTOR

In order to gain some idea of the nature of this injurious factor, a series of tests were carried out. In these experiments only dried white birch wood was used. The wood was chopped to coarse chips and these were then ground in a mill to a coarse sawdust that would pass a ten-mesh sieve. In the tumbler experiments, 80-mesh sawdust, obtained by rasping the wood with a fine rasp, was used. In the greenhouse experiments, 2-gallon jars with side bottom drainage were used. All experiments were conducted at 25 per cent moisture content which was kept constant by weighing at regular intervals and adding the necessary amount of distilled water. The lime used was a natural limestone of about 106 per cent calcium carbonate equivalent and passed an 80-mesh sieve. The manure was well-rotted horse manure and had passed a $\frac{1}{4}$-inch screen. It contained very little straw.

The effect of sawdust on the growth of oats

In this series, lime, manure, and lime with manure were added to the soil with the sawdust, and a study made of the effect on the growth of the oats and the nitrate content of the soil. After the oats were planted, the jars were made up to the required moisture content. When the seedlings were about three inches high, they were thinned so that each jar had fifteen plants.

During the first two weeks no differences could be noticed between the plants where sawdust was present and those where none was present. At

the end of this time, however, the plants in the jars treated with sawdust began to develop a yellow color, the stems and leaves were thin and rigid and towards the end of the experiment they became badly infected with rust. The plants in the untreated jars were healthy, succulent and of a good color. In the soil containing sawdust, very little response to the addition of lime, manure, or lime with manure was obtained; while in the untreated soil very good responses were obtained especially with both lime and manure. The plants were cut after nine weeks and soil samples taken the same day and analyzed for nitrate. The results are shown in table 3.

At the end of the experiment no nitrates were present in the soil which had received wood. The dry weights of the plants grown in the presence of wood were less than those of the plants grown in the absence of wood.

From these results it appears that the depression in the growth of the oats was due to a lack of nitrate nitrogen rather than to any toxic constituents in the wood.

TABLE 3

The effect of sawdust on the growth of oats and the nitrate content of the soil

NUMBER	TREATMENT*	NITROGEN AS NITRATE IN 100 GM. DRY SOIL	DRY WEIGHT OF PLANTS
		mgm.	*gm.*
1	Untreated, control..............................	2.13	5.2
2	80 gm. wood...................................	0.00	3.2
3	16 gm. lime...................................	5.65	8.0
4	16 gm. lime, 80 gm. wood......................	0.00	3.6
5	80 gm. manure.................................	2.73	8.5
6	80 gm. manure, 80 gm. wood	0.00	4.2
7	16 gm. lime, 80 gm. manure.....................	8.62	10.5
8	16 gm. lime, 80 gm. manure and 80 gm. wood......	0.00	4.8

* 8 kilograms of soil in each jar.

The effect of wood pulp cellulose on the growth of oats and the nitrate content of the jars

This experiment was the same as the preceding in all respects, except that Carrington silt loam was used instead of Colby silt loam. The wood was replaced by wood pulp cellulose obtained from spruce by the Burgess process. The pulp was extracted with warm 5 per cent hydrochloric acid before it was incorporated into the soil, and then washed with several changes of boiling water. In this way it was hoped that the possibility of toxic wood constituents would be removed, and any depression in the growth would be due to the lack of nitrate or to the toxic action of cellulose decomposition products rather than toxic bodies of the wood.

Very early in the experiment there was a marked depression on the plants growing in the soil which had received the cellulose. Here the plants showed the same peculiarities as with the wood, but to a much more marked degree.

There was very little response to lime, manure, or lime with manure, while on the untreated soil these substances proved most beneficial. When the plants on the treated soil had reached a height of about six inches they became so infected with rust that the experiment had to be discontinued. The stems and leaves were thin and rigid and had a yellow color typical of nitrate starvation. The dry weights of the plants and the nitrate content of the soil are given in table 4. Here again it is noticed that the soil which had been treated with cellulose contained no nitrate. The phenoldisulfonic reagent did not give the slightest color. These results agree with those of Koch who found that soil which contained 0.33 per cent of filter paper contained no nitrate nitrogen. The soil had recuperated after eighteen months and he could find nitrate again. This experiment leaves no doubt about the fact that the lack of nitrate is due to the cellulose decomposition. That this lack is actually. due to a reduction is shown by the following experiment.

TABLE 4

The effect of wood pulp cellulose on the growth of oats and the nitrate content of the soil

NUMBER	TREATMENT*	NITROGEN AS NITRATE IN 100 GM. DRY SOIL	DRY WEIGHT OF PLANTS
		mgm.	*gm.*
1	Untreated, control..............................	3.24	9.7
2	100 gm. cellulose................................	0.00	2.4
3	16 gm. lime......................................	4.83	10.0
4	16 gm. lime, 100 gm. cellulose...................	0.00	2.3
5	80 gm. manure...................................	3.78	12.1
6	80 gm. manure, 100 gm. cellulose.................	0.00	2.6
7	16 gm. lime, 80 gm. manure.....................	8.94	18.2
8	16 gm. lime, 80 gm. manure, 100 gm. cellulose.......	0.00	2.7

* 8 kilograms of soil per jar.

The reduction of nitrate in the soil by cellulose and sawdust

To show on a definitely quantitative basis that wood and cellulose can reduce nitrate in the soil, an experiment was carried out in tumblers of soil in the laboratory. A garden soil containing 50–60 parts per million of nitrate nitrogen was used. The exact nitrate content of the soil was measured and the wood and cellulose added in varying amounts. The wood was added as 80-mesh sawdust and the cellulose as absorbent cotton which had been cut to a fine state with a pair of scissors. The tumblers were kept at 25 per cent moisture content, room temperature, and covered with petri dishes.

At the beginning of the experiment the soil contained 5.31 mgm. nitrate nitrogen per 100 gm. dry soil. The results after four weeks are given in table 5. The control gained very little during the four weeks and 0.25 per cent cellulose was enough to reduce all the nitrate during that time. In the case of the wood 0.25 per cent reduced the nitrate about 50 per cent, while 0.5 per cent was enough to completely destroy it.

The effect of sawdust on the nitrification of bloodmeal

A study was made of the effect of wood on the nitrification of an easily nitrifiable substance such as blood meal. The amounts added are much larger than what would be added under field conditions. The experiment was carried out under the same conditions as former tests. An untreated soil blank was run as a control, one contained no wood, and the soil in the other tumblers contained 0.5 gm. bloodmeal together with varying amounts of wood as 80-mesh sawdust. After four weeks the tumblers were all analyzed for nitrate.

TABLE 5

The reduction of nitrate by cellulose and sawdust

NUMBER	TREATMENT	NITRATE NITROGEN PER 100 GM. DRY SOIL
		mgm.
1	Untreated, control	5.31
2	0.25 per cent cellulose	0.00
3	0.5 per cent cellulose	0.00
4	0.25 per cent sawdust	`2.53
5	0.5 per cent sawdust	0.00
6	1.0 per cent sawdust	0.00

TABLE 6

The effect of sawdust on the nitrification of bloodmeal

TUMBLER NUMBER	TREATMENT OF 100 GM. SOIL	N AS NO_3 IN 100 GM. DRY SOIL	AMOUNT OF BLOODMEAL NITRIFIED
		mgm.	*per cent*
1	Untreated, control	6.60	
2	0.5 gm. blood meal	51.36	59.7
3	0.5 gm. blood meal, 0.25 gm. sawdust	42.92	47.9
4	0.5 gm. blood meal, 0.5 gm. sawdust	33.40	35.3
5	0.5 gm. blood meal, 1.0 gm. sawdust	30.00	30.8
6	0.5 gm. blood meal, 2.0 gm. sawdust	23.10	21.8

From the results in table 6 it is seen that the wood depresses nitrate accumulation to a very marked degree. The control containing neither wood nor bloodmeal gained very little in nitrate, while the blank containing only bloodmeal made a considerable gain. The soil at the beginning of the experiment contained 6.37 mgm. nitrate nitrogen per 100 gm. dry soil.

The effect on sawdust on the growth of inoculated peas

Since the depression caused by the presence of sawdust was, as far as could be seen, due to the lack of nitrate, it should be possible to grow peas in the presence of sawdust, without their suffering any ill effects, provided they could be inoculated and a liberal supply of lime were present.

To test this out, the peas were grown in half-gallon jars containing 3 kgm. white quartz sand.   A Hopkins and Pettit solution with nitrogen omitted was added as a source of nutrient salts.   At the beginning of the experiment each jar received 500 cc. of the solution and three weeks later an additional 500 cc.   Jars 1 and 2 received 30 gm. of lime; jars 3 and 4 received the same amount of lime plus 30 gm. of sawdust.   The seeds were germinated in moist sand and seedlings of the same size and strength transplanted into the jars and inoculated at once.   Each jar contained four plants.

During the entire time of the experiment no differences between the two sets of plants could be noticed.   They were of the same size and color.

This experiment and also the results of table 2 indicate that there is no appreciable toxic effect due to the wood constituents.   Both sets showed good inoculation and since they could provide for their own nitrogen they did not suffer from the lack of nitrate.

TABLE 7

The effect of sawdust on the nitrate accumulation in soil treated with bloodmeal and lime

AGE OF CULTURE	NITRATE NITROGEN PER 100 GM. DRY SOIL	
	With wood	Without wood
days	*mgm.*	*mgm.*
0	2.08	2.08
2	1.44	2.08
4	1.69	2.08
7	1.69	2.08
14	5.55	8.67
21	12.7	31.20
28	19.68	39.00
35	24.96	40.04
42	26.69	
49	31.55	47.14
56	40.21	57.20
128	44.7	58.48

The effect of sawdust on the accumulation of nitrate in the soil from the nitrification of bloodmeal

In this experiment the accumulation of nitrate from an easily nitrifiable substance in the form of bloodmeal was studied for a considerable length of time in soil treated with lime and wood.   A large number of flasks containing 200 gms. of a cropped Colby silt loam, 1 gm. of bloodmeal, 2 gms. of lime, and 2 gms. of sawdust, were set up together with a number of blanks without saw-dust.   These were kept at 25 per cent moisture content and at room temperature.   To insure optimum aeration the contents of each flask were stirred after one week.   Nitrates were determined after 2, 4, and 7 days and after that time at the end of every week.   Duplicate flasks were analyzed and good checks were obtained.

The results are seen in table 7. During the entire duration of the experiment the nitrate in the flasks with the wood was considerably lower than in the blanks. Towards the end there seemed to be some recovery. Koch (6) also found a recovery in jars treated with filter paper. After eight months he found no nitrate in soil which at the beginning contained nitrate; after eighteen months he again found up to 20 parts per million of nitrate nitrogen. This recovery is undoubtedly due to a diminution in the amount of cellulose present. Charpentier (2) found that in cylinders where he had added 1 per cent of cellulose to the soil, 70 per cent of the added cellulose had disappeared after twenty-eight weeks. In the case of the sawdust the recovery would be much more rapid, because the cellulose material is comparatively inaccessable and the large amounts of organic nitrogen in the form of bloodmeal would hasten the decomposition, as was found by Charpentier (2).

With such high amounts of nitrifiable organic matter present as in this experiment, the rate of nitrification was undoubtedly much greater than the rate of reduction, and since the reduction decreased with the cellulose available, towards the end it was very small and a much larger accumulation of nitrates resulted.

SUMMARY

The foregoing experiments show that the unfavorable action of wood on plant growth is due to a lack of nitrate in the soil. This loss of nitrate nitrogen is no doubt due to the great increase in the assimilation of nitrates by microörganisms. Since the same results can be obtained with wood-pulp cellulose as with wood, it does not seem likely that there is any toxic action on the plant due to such wood constituents as essential oils, resins, and tannins. When added in large amounts, Koch (7) showed that these substances are toxic to plants, however, the white birch used in this investigation only contained about 2.5 per cent tannin and the other constituents in even lesser amounts. The very small amounts of these substances derived from the added wood (1 per cent) could hardly have any appreciable effect on the growth of plants.

Certain kinds of wood, for example, alder or poplar, are more injurious than birch or willow. This difference is due perhaps to the variation in rate of decomposition. The alder and poplar are decomposed more slowly than the other woods, and hence their injurious effect is noted for a longer time.

Since inoculated peas can be grown in the presence of sawdust without showing any ill effects, it seems that the injury from wood cannot be due to the presence of a poisonous substance.

The experiments also show that the lack of nitrate is due to a reduction rather than to an inhibition of nitrification, and that this reduction is caused by a group of organisms which make use of cellulose. No evidence has been obtained as to which group is responsible for this reduction. It may be due

to the organisms which decompose cellulose directly, or to those groups which live on its fermentation products.

That nitrification takes place is shown by the fact that with large amounts of bloodmeal in the soil the rate of nitrification can be so increased that it exceeds the rate of reduction and an accumulation of nitrate takes place.

The results of these tests taken as a whole indicate that the reduced growth of plants following the application of young wood is closely connected with a loss of nitrates. This injury soon passes off and the following season is almost without effect.

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FIG. 1 THE EFFECT OF BIRCH ON OATS

Jar 1.   Control, no birch
Jar 2   225 gm. coarse birch
Jar 3.   450 gm. coarse birch
Jar 4.   450 gm. fine birch
Jar 5.   Ashes from 450 gm. birch
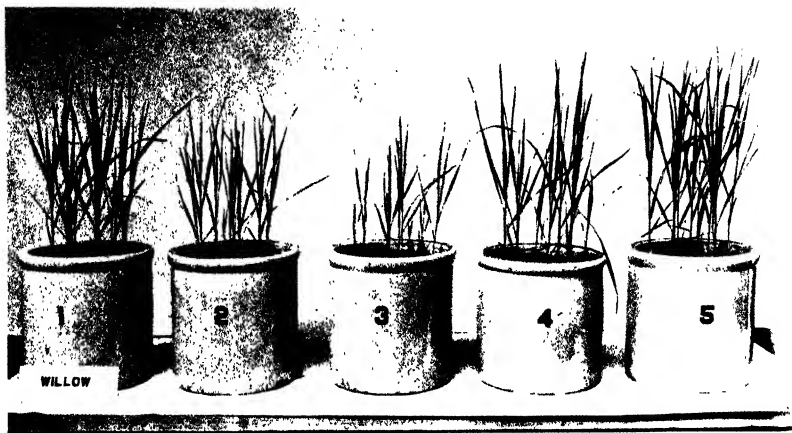
FIG. 2 THE EFFECT OF WILLOW ON OATS

Jar. 1   Control, no willow
Jar 2.   225 gm coarse willow
Jar 3.   450 gm. coarse willow
Jar 4.   450 gm. fine willow
Jar 5.   Ashes from 450 gm. willow

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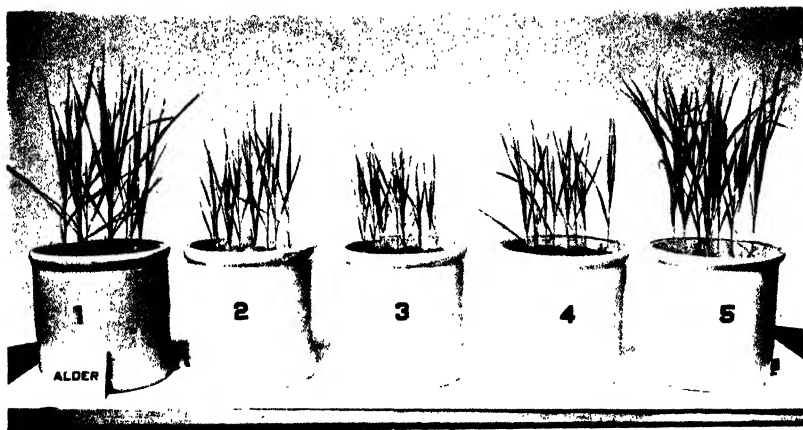
FIG. 1. THE EFFECT OF ALDER ON OATS

Jar 1.   Control, no alder
Jar 2.   225 gm. coarse alder
Jar 3.   450 gm. coarse alder
Jar 4.   450 gm. fine alder
Jar 5.   Ashes from 450 gm. alder
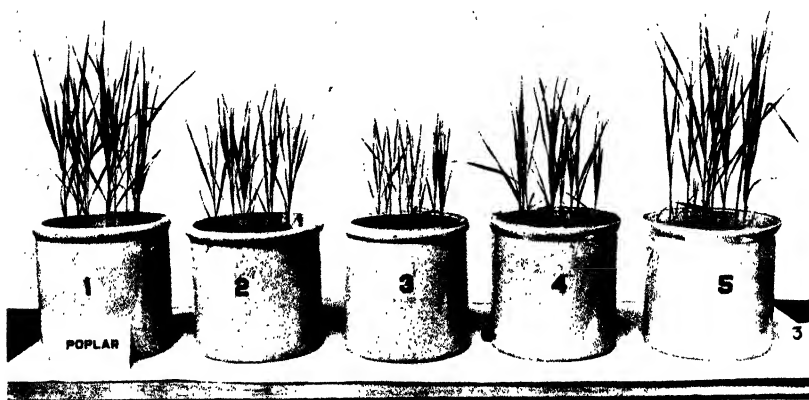
FIG. 2. THE EFFECT OF POPLAR ON OATS

Jar 1.   Control, no poplar
Jar 2.   225 gm. coarse poplar
Jar 3.   450 gm. coarse poplar
Jar 4.   450 gm. fine poplar
Jar 5.   Ashes from 450 gm. poplar
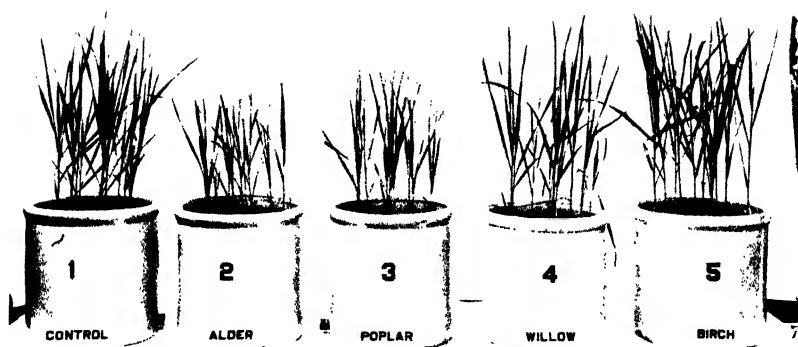
THE EFFECT OF VARIOUS KINDS OF WOOD ON THE GROWTH OF OATS

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EASILY SOLUBLE CALCIUM OF THE SOIL IN RELATION TO ACIDITY AND RETURNS FROM LIMING[1]

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The work reported in this paper was carried out for the purpose of studying the relation between the easily soluble calcium in the soil and the returns obtained from the use of lime in the field. It was hoped that some information might be gained which would help to explain further why certain strongly acid soils are able to produce good yields of all the common farm crops including red clover and alfalfa, while on the other hand some slightly acid soils may require liming before satisfactory crops can be grown. It is a vital question whether there are not other factors that may in many cases assume an importance quite as great as the acidity itself in determining the need of a soil for lime.

Conner (5) and others have called attention to the effect of soluble aluminum in certain soils. Truog (26) points out that it may be largely a matter of the ability of the plant to get the calcium necessary for its own development. He has called attention to the difference in the feeding power of different crops for calcium. It would seem from this that the amount of soluble calcium in some form in the soil or soil solution may be of great significance in furnishing to a particular crop the amount of this element which it needs. This more or less readily soluble calcium may be of importance in making other necessary elements "physiologically available" as has been shown by True (23 and 24). Hoagland (9) has also pointed out that substances may be absorbed at different rates under varying hydrogen-ion concentrations, even with equal total salt concentrations. Bryan (4) found greater amounts of calcium in alfalfa and clover plants grown in nutrient solutions with low hydrogen-ion concentrations. McCall (13) concludes after reviewing some of the more recent work on soil acidity, that the common opinion that the application of lime must be carried to the point of neutralization, must be revised and modified, in view of the fact that many crops make satisfactory growth on soils which are regarded as acid.

Wolff (29) showed as early as 1871 that the amount of calcium found in plants of different species varied between wide limits and the range was quite marked even in the same species, when grown under different conditions. White (28) found that red clover and sorrel increased

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in content of calcium when limestone was added to soil from the Pennsylvania plots, having an indicated lime requirement of 5200 pounds an acre.

Petrographic examinations of soils by Plummer (19) demonstrated the existence of calcium in soils in a number of different minerals, particularly the silicates. This work was substantiated by Shorey, Fry, and Hazen (21) and they further demonstrated that some of the calcium silicates are easily soluble in a weak acid, while others resist the action of stronger acids. Their data show that in many cases soils with approximately the same total calcium content may vary widely in the amount of calcium existing as easily soluble silicates. Ames and Gaither (2) found that the percentage of calcium soluble in 0.2 N HNO$_3$ varied from 1.1 per cent to 88.7 per cent of the total calcium found in two different sandy loams.

Ames (1) showed that when dried blood was nitrified in an acid silt loam soil the amount of water soluble calcium was greatly increased.

MacIntire and Willis (11), Conner (5), Hartwell and Pember (7) and Mieth (15) showed that plants may very readily and efficiently obtain their calcium from silicates.

Holleman (10), Mitscherlich (16), Engels (6), Maschhaupt (12) and Shedd (20), studied the effect of carbonated water upon the solubility of the calcium of the soil.

Ames and Schollenberger (3) state that in some soils there was a fairly good relation between the calcium and magnesium soluble in 0.2 N HNO$_3$ and the Truog acidity test.

PLAN OF INVESTIGATION

Since a large part of the work on the subject of soil acidity has been done in the laboratory and since, on the other hand, the actual need of a particular soil for lime has usually been determined by field tests, it seemed desirable to correlate in a more definite way some of the results of these two methods of experimentation. It was planned to work, for the most part, with soils in which the need for lime treatment in the field had been more or less definitely determined by experiment, since the final test of a soil's need for lime must be made in the field. Samples from the untreated and limed portions of these experimental fields were collected and brought to the laboratory for analysis. Determinations were made of various factors which might have a bearing upon, or help to explain, the results obtained from the use of lime in the field. For most of the soils these determinations consisted of the following:

Total calcium, Total magnesium, Calcium content of the soil solution, Calcium soluble in 0.04 N carbonated water, Soil acidity by the Truog test, Total nitrogen and total phosphorus; the H-ion concentration of the displaced soil solution, (on the greenhouse soils), Calcium soluble in 0.20 N HNO$_3$.

A few soils for this work were collected in the autumn of 1921 for pot tests and for use in perfecting the methods to be used in the latter part of this study. The soils collected at this time consisted of Carrington silt loam and virgin and cropped Miami silt loam from the Keyser Farm near Madison, Wisconsin. The others were Plainfield sand and Colby silt loam from the Hancock and Marshfield substations in central Wisconsin.

In May, 1922, samples of soil were collected from fields in Wisconsin where the results of liming had been demonstrated. These samples were taken to a depth of seven inches and were collected in paraffined paper bags. A part

of each sample was used for displacement of the soil solution, and the remainder dried in the greenhouse for a determination of the calcium soluble in 0.04 N carbonated water. In addition to the soil samples from Wisconsin, other samples were collected from several of the soils experiment fields in Missouri.

EXPERIMENTAL WORK

In the first part of this paper will be reported the determinations made upon the soil solution. The method used in obtaining this soil solution was practically the same as that described by Parker (18). The calcium determinations were made on a 50-cc. sample of the displaced soil solution.

TABLE 1

Effect of liming upon the calcium content of the soil solution—samples taken in the spring of 1922

LAB. NO.	LOCATION	SOIL TYPE	CA PER ACRE IN SOIL SOLUTION*		INCREASE DUE TO LIME
			Not limed	Limed	
			lbs.	lbs.	lbs.
	Missouri				
207, 208	Windsor	Oswego silt loam	15.2	19.5	4.3
	Wisconsin				
236, 237	Shawano County	Not determined	40.3	42.4	2.1
238, 239	Shawano County	Not determined	36.6	42.4	5.8
241, 242	Janesville	Waukesha silt loam	26.5	40.0	13.5
250, 251	Stockton	Sand knoll	6.1	8.2	2.1
252, 253	Stockton	Plainfield sandy loam	11.3	6.1	−5.2
274, 275	Plover	Waukesha sand (1)	11.3	7.6	−3.7
274, 276	Plover	Waukesha sand (2)	11.3	11.0	−0.3
278, 283	Hancock	Plainfield sand	6.3	9.5	3.2
279, 281	Hancock	Plainfield sand	7.1	8.7	1.6
286, 287	Neilsville	Colby silt loam (rolling phase)	18.6	39.0	20.4
289, 290	Almond	Plainfield sandy loam	15.6	28.1	12.5
291, 292	Neilsville	Vesper fine sandy loam	18.8	44.4	25.6
Average...			17.3	23.6	6.3

* All calculations are made on basis of 2,000,000 pounds of dry soil per acre.

EFFECT OF LIMING

Liming slightly increased the calcium content of the soil solution as shown by table 1. On only two of the twelve soils shown in this table is the reverse true. It is difficult to explain these two exceptions to the general rule. It seems probable, however, that since the calcium content of these sandy soils was low and the clover or alfalfa crop fairly heavy, the apparent decrease from lime had really been absorbed by the crop. This assumption is supported by the results shown in table 3, where the calcium absorbed by the clover is greater than the decrease found in the soils shown in table 1. In

table 2 the effect of lime in conjunction with fertilizers is shown. It may be seen from this table that there are three cases out of nine where the limed land had less calcium in solution than did the unlimed. This again is probably due to a greater absorption by the crop on these plots.

The calcium in the soil solution varies widely under different conditions in the same soil. The results shown in tables 1, 2 and 3 are from samples taken during the spring of 1922. If the amount 37.6 pounds of calcium per acre in solution shown in table 3 for untreated Colby silt loam is compared with the soluble calcium in the same soil kept in the greenhouse for six months (table 4), it will be seen that there is a difference of 279.2 pounds. This is

TABLE 2

Effect of lime in conjunction with manure or fertilizer upon the calcium content of the soil solution

LAB. NO.	LOCATION	SOIL TYPE	MANURED OR FERTILIZED LAND. Ca PER ACRE IN SOIL SOLUTION		INCREASE DUE TO LIME
			No lime	Limed	
			lbs.	*lbs.*	*lbs.*
	Missouri				
229, 219	Strafford	Lebanon silt loam	29.4	33.6	4.2
224, 223	Willow Springs	Clarksville silt loam	22.8	27.8	5.0
225, 223	Willow Springs	Clarksville silt loam	29.9	27.8	−2.1
234, 233	Cuba	Lebanon silt loam	14.7	21.1	6.4
150, 151	Maryville	Marshall silt loam	36.0	58.6	22.6
	Wisconsin				
245, 246	Janesville	Waukesha silt loam	32.8	27.7	−5.1
265, 262	Marshfield	Colby silt loam	32.4	42.6	10.2
272, 273	Coddington	Peat	57.9	51.4	−6.5
281, 282	Hancock	Plainfield sand	5.5	9.1	3.6
Average..			29.0	33.3	4.2

* Samples taken in spring 1922.

due to the fact that the latter sample was collected in the fall of 1921 and kept in the greenhouse until March 3, 1922. The other sample which had only 37.6 pounds calcium in the soil solution was collected May 20, 1922, after it had received numerous spring rains and was supporting a good growth of clover. According to the results of McCool and Millar (14) it would seem that the percolation of rain water has carried the calcium salts downward into the subsoil below the top 7-inch layer and probably has leached much of it entirely from the soil. The calcium in solution in the greenhouse soils may also have been increased by the drying of these soils, before the crop was started.

EFFECT OF THE CROP UPON THE CALCIUM CONTENT OF THE SOIL SOLUTION

Hoagland (8) has shown by measuring the depression of the freezing point that a crop materially reduces the total amount of salts in the soil solution. That the crop absorbs calcium from the soil solution to an extent that can be measured in the displaced soil solution may be seen from table 3, where land having a rank growth of clover is compared with similar land having no crop, or which had just recently been planted to a spring crop. Sample 259 was taken from near the centre of the bare spots where the clover had been killed the previous year by the grain shocks. Sample 258 was taken from the clover land only a few feet away from sample 259. There was approximately two tons of clover hay per acre on the land at this time, May 20, 1922. When the crop was harvested about the middle of June the yield was three

TABLE 3

Effect of clover growth upon the calcium content of the soil solution

LAB. NO.	SOIL TREATMENT*	Ca PER ACRE IN THE SOIL SOLUTION		Ca TAKEN FROM SOIL SOLUTION BY CROP
		Clover land	Uncropped land	
		lbs.	*lbs.*	*lbs.*
258	Clover field, new farm. Good clover	44.4		
259	Same field. Bare spots under shocks		57.3	12.9
256	Agronomy plot. Corn just planted		72.7	28.3
257	Series 800. Land plowed		67.6	23.2
260	Plot 102A. Good clover (check)	37.6		
266	Plot 202A. Barley just coming up		82.6	45.0
265	Plot 108A. Clover (manure Rock Phos.)	32.4		
267	Plot 208A. Barley up (manure Rock Phos.)		53.7	21.3

* Soil type was Colby silt loam, Marshfield, Wis. Substation.

and one-half tons per acre. Samples 256 and 257 were from a different field, but the land had received approximately the same soil treatments as 258. None of this soil had been limed. These, together with the other results given in table 3 show that the crop had reduced the amount of calcium in the soil solution by 22.5 per cent in sample 258; 54.4 per cent in sample 260; and 39.6 per cent in sample 265. It seems evident from these results that the calcium content of the soil solution may not only be very greatly reduced during certain seasons of the year by the action of percolating water, but that a still further reduction takes place because of the absorption by a rapidly growing crop.

This effect of the crop is still further shown by the results recorded in table 4. These figures were obtained from soils kept in the greenhouse. A crop of corn was harvested from all soils on February 2, 1922. The soil from one of each pair of 2-gallon jars was removed, thoroughly mixed and a sample taken for a calcium determination on the soil solution. The duplicate jar was kept

at optimum moisture content for two months. On March 3, 1922, soy-beans were harvested from other pots containing these same soils. One of each pair of duplicates was sampled and analyzed as described above, and the other was allowed to stand under optimum conditions until April 3, 1922 when all of the remaining duplicate pots from both the corn and soybean series were sampled as before and the calcium in the soil solution determined. The results of the first and second determinations are shown in table 4. With but one exception there was a decided increase in the calcium in solution after standing one or two months. Some calcium is probably made soluble from the silicates by simple hydrolysis and some is dissolved by the action of car-

TABLE 4

Effect of soil standing after crop is harvested, upon the calcium content of the soil solution

POT NO.	SOIL TYPE	FIELD TREATMENT	GREENHOUSE CROP	Ca PER ACRE IN SOIL SOLUTION		GAIN AFTER FIRST TRIAL	TIME SINCE HARVEST
				First determination	Second determination		
				lbs.	*lbs.*	*lbs.*	*months*
13–14	Carrington silt loam	General farm	Corn	33.0	82.8	49.8	2
31–32	Miami silt loam	Cropped	Corn	15.0	48.4	33.4	2
45–46	Miami silt loam	Virgin	Corn	10.0	46.4	36.4	2
65–66	Colby silt loam	Virgin	Corn	126.6	181.8	55.2	2
77–78	Colby silt loam	Manure lime	Corn	265.0	259.2	−5.8	2
89–90	Colby silt loam	Lime (1921)	Corn	163.8	191.2	27.4	2
101–102	Plainfield sand	No treatment	Corn	7.8	38.4	30.6	2
113–114	Plainfield sand	Limed	Corn	4.6	21.0	16.4	2
17–18	Carrington silt loam	General farm	Soybeans	44.4	84.0	39.6	1
57–58	Colby silt loam	No treatment	Soybeans	316.8	349.6	32.8	1
69–70	Colby silt loam	Virgin	Soybeans	91.0	170.4	79.4	1
81–82	Colby silt loam	Manure lime	Soybeans	260.6	266.6	6.0	1
Average..				111.5	145.0	33.4	

Corn harvested Feb. 2, and Soybeans March 3, 1922. Second determination April 3, 1922.

bon dioxide in solution, as well as by other soil acids. It will be seen that the greatest increases were for the most part in the acid soil. A part of it may also have been due to the decay of roots from the crop which had just been harvested. The large amount of calcium in the soil solution of these greenhouse soils as compared with the field samples indicates that there is a very marked increase due to long standing under moist, warm conditions, where no leaching can take place.

STUDIES ON GREENHOUSE SOILS

A few soils kept in the greenhouse during the winter of 1921 and 1922 were not only analyzed for the total calcium and the calcium in the soil solu-tion, but also for the amount of this element soluble in 0.2 N HNO$_3$ and

0.04 N carbonated water. They were also tested for acidity by the Truog test and for hydrogen-ion concentration by the colorimetric method. These soils were used chiefly as preliminary material before beginning the work with the samples from the field, but since they include some determinations not made on the field samples the results are presented for comparison.

Table 5 shows the amount of calcium of different degrees of solubility in the several soils kept in the greenhouse. The figures on the soil solution show the amount of calcium that has been already dissolved. The amount of calcium soluble in 0.04 N carbonated water probably includes that reported in the soil solution and nearly all the calcium in carbonate form, except in the case of limed soils where there may be some fairly large pieces of limestone which would not be completely dissolved. Some of the calcium in the form of easily soluble silicates is also dissolved by this carbonated water and changed

TABLE 5

Calcium content and acidity of different soils after being kept in the greenhouse for four months

POT NO.	SOIL TYPE	TREATMENT	TOTAL Ca PER ACRE	CALCIUM PER ACRE SOLUBLE IN			REAC-TION OF SOIL SOLU-TION †	ACIDITY TRUOG TEST ‡
				0.2 N HNO$_3$	.04 N H$_2$CO$_3$	Soil solu-tion		
			lbs.	*lbs.*	*lbs.*	*lbs.*	*pH*	
13	Carrington silt loam	None	12,460	5290	760	33.0	5.8	3
31	Miami silt loam	Cropped	13,500	4600	1000	15.0	6.6	1+
45	Miami silt loam	Virgin		4520	1000	10.0	6.3	2+
53	Colby silt loam	None	12,600	4740	930	241.4	5.6	4—
65	Colby silt loam	Virgin	14,000	2660	710	126.6	4.8	5
77	Colby silt loam	Manure, lime	15,000*	5700	1260	265.0	6.3	2+
89	Colby silt loam	Limed	13,000*	5670	1100	163.8	6.6	2+
101	Plainfield sand	None	10,900	1200	540	7.8	5.8	2+
113	Plainfield sand	Limed	12,500*	1910	896	4.6	6.6	1—

* Increase over unlimed estimated from amount of application.

† Determined by colorimetric method.

‡ 1. Very slight acidity, 2. slight, 3. medium, 4. Strong, 5. Very strong.

to a bicarbonate. It is quite significant that there is no relation between the calcium soluble in 0.04 N carbonated water and the amount found in the soil solution. In table 5 it may be seen that the untreated Colby silt loam showed a much higher amount of calcium in the soil solution, but a lower amount in the carbonated water extract than did the Miami silt loam. The former soil is derived mainly from granite rocks while the latter is a glacial soil and largely of limestone origin.

SOLUBLE CALCIUM AND ACIDITY OF GREENHOUSE SOILS

The relation of acidity to the amount of calcium in solution seems also to be an important factor. In the Colby silt loam the acidity was strong to very strong by the Truog test, and the hydrogen-ion concentration of the soil

solution showed a pH value of 4.8 to 5.6.   The calcium in the soil solution
was 241.4 pounds per acre in the check and 126.6 in the virgin soil.   With
the untreated Miami soils the acidity was only very slight and the pH value
was 6.3 and 6.6.   The calcium in solution was only 10 and 15 pounds an
acre.   It would seem from these data and those given in table 4 that the
higher acidity of the Colby soils may be a factor in dissolving some of the
calcium in the more easily soluble silicates, thus bringing it into the soil
solution.   It should also be noted that in all cases where the calcium in the
soil solution is low the acidity is also low.   It is only in the case of the Colby
silt loam which has received lime that we have a high amount of calcium
in solution and only a little more than slight acidity.   The Plainfield sand
receiving lime showed a very low amount of calcium in solution, but this can
probably be accounted for by the increased demands of the crop, since the
amount of calcium in solution is normally very low in this soil.   Table 4 shows
that after the removal of the crop the calcium in solution in this soil was
materially increased.   The calcium soluble in 0.04 N carbonated water and
0.2 N HNO_3 is considerably higher in all soils used in the greenhouse where
lime has been applied than in the unlimed soil.

The method of making 0.2 N HNO_3 extractions was essentially the same as
used by Ames and Gaither (2).   No very good correlation was found between
the calcium soluble in 0.2 N HNO_3 and the response to lime in the field.

CARBONATED WATER EXTRACTIONS

The second part of this study was concerned with the relation between
the amount of easily soluble calcium and the returns obtained by the use of
lime in the field.   The chemical methods used in this work are essentially
as given in an unpublished article by Professor E. Truog of the University
of Wisconsin.

The calcium was determined on duplicate aliquot samples obtained by
shaking 12 gm. of soil with 600 cc. of 0.04 N carbonated water for two hours
and then filtering to obtain a clear solution.

THE RELATION OF FERTILITY AND SOLUBLE CALCIUM CONTENT TO THE USE OF LIME IN THE FIELD

It has been a common observation among farmers and experiment station
men that many soils, acid by all the common tests, produce all the ordinary
field crops satisfactorily and do not give large increases in crop yields following
applications of lime.   The reasons for this have not been well known and
has often been the cause of disappointment when lime has been applied on
certain acid soils.   This has caused many to put less dependence than for-
merly in the ordinary acidity tests, especially since there has not been satis-
factory agreement in the results obtained by different methods.   Some have
hesitated to recommend too freely the use of lime simply on the basis of acidity

determinations. There has been a general impression that the returns from lime depend somewhat on the general fertility of the land, but just how, is not definitely known.

TABLE 6

Relation of general fertility and the amount of calcium soluble in .04 N carbonated water to the response of soils to lime in the field

(Soils giving good returns for liming)

LAB. NO.	LOCATION	SOIL TYPE	ACIDITY TRUOG TEST	Ca PER ACRE SOLUBLE IN .04 N H_2CO_3	PLANT FOOD CONSTITUENTS PER ACRE	
					Nitrogen	Phosphorus
				lbs.	*lbs.*	*lbs.*
306, 307	St. James, Mo.	Gerald silt loam	4+	494	2765	654
298, 299	Windsor, Mo.	Oswego silt loam	4	574	2060	710
300, 301	Cuba, Mo.	Lebanon silt loam	3+	570	1630	580
302, 303	Strafford, Mo.	Lebanon silt loam	3	510	1710	620
410, 411	Union, Mo.	Union silt loam	3	540	1600*	700
350, 351	Hancock, Wis.	Plainfield sand	2+	620	785	742
360, 361	Hancock, Wis.	Plainfield sand So. Field	2+	566	785†	360
Average.............................			3+	553	1619	624

* Average of ten analyses of this type.

† Analysis of No. 350 used.

TABLE 7

Relation of general fertility and .04 N H₂CO₃ soluble calcium content to the response of soils to liming

(Soils giving medium to small returns for lime)

LAB. NO.	LOCATION	SOIL TYPE	ACIDITY TRUOG TEST	Ca PER ACRE SOLUBLE IN .04 N H_2CO_3	PLANT FOOD CONSTITUENTS PER ACRE	
					Nitrogen	Phosphorus
				lbs.	*lbs.*	*lbs.*
336, 337	Janesville, Wis.	Waukesha silt loam	4+	880	5385	1480
116, 117	Maryville, Mo.	Marshall silt loam	3+	730	3965	1210
334, 335	Columbia, Mo.	Putnam silt loam	3+	830	2610	1030
332, 333	Janesville, Wis.	Waukesha silt loam	3+	820	4074	1280
416, 417	Marshfield, Wis.	Colby silt loam (202A)	3	800	4982	1448
342, 343	Coddington, Wis.	Peat	2+	2570	9820	3020
308, 309	Willow Springs, Mo.	Clarksville silt loam	2	800	1400	240
Average..........................			3	1061	4605	1387
Average without peat soil.....................			3+	810	3736	1114

In table 6 will be found a list of several soils that have usually given what would be called good returns for liming. That is, the results of field experiments show that it could be considered a profitable farm practice on such

lands. The results shown in these tables were obtained from the untreated plots, adjoining those that had been limed, and with which they were compared in yield. The acidity of these soils according to the Truog test; the nitrogen and phosphorus content; and the amount of calcium soluble in 0.04 N carbonated water are given in the table. Similar data for several soils that have given in comparative field experiments smaller returns for liming, in most cases below the cost of treatment, are given in table 7.

These figures would indicate that in the soils here considered, it is those low in potential fertility and low in easily soluble calcium that have given the most satisfactory returns for lime. It should be noted too that the average acidity of the two sets of soils is practically the same. It is the other factors that differ widely. The soils giving small returns for lime show a decidedly higher content of easily soluble calcium, 1061 pounds an acre as compared with 553 in the soils giving good returns. It would seem reasonable from this that they should act as they do in giving smaller increases for additional applications of lime than the soils which are decidedly lower in the amount of this easily soluble material.

It must not be assumed from these tables that soil acidity has no effect upon crop growth, or that the more acid portions of the same soil will produce as good crops as areas of less acidity. The fact is that the soils here reported are widely different in their physical and chemical composition. It is under conditions of this sort, that the other factors which go to make up the fertilty may overbalance to a certain extent the single factor of acidity in determining the need of different soils for lime. It is just at this point where the ordinary acidity tests fall short as a reliable method for determining in the laboratory soils where lime will be most likely to give profitable returns. Until the other physical and chemical properties, as well as the acidity of a soil are given due consideration, it will be impossible to make accurate recommendations on the basis of laboratory tests for the practical use of lime in the field.

EFFECT OF FERTILITY

In tables 6 and 7 can be seen the comparison between the nitrogen and phosphorus contents of the soils giving large and small returns for liming. It will be seen that in most cases in the soils here studied where there is a good supply of nitrogen and phosphorus the soils have not given large increases from the use of lime. In the soils listed as giving good returns for lime, only two had as much as 2000 pounds nitrogen an acre and none showed a phosphorus content of 800 pounds an acre. The Clarksville silt loam appears to be an exception to the general rule, in that it has a low nitrogen and phosphorus content and has given only small increases for lime. This can probably be explained by the fact that this soil showed 800 pounds of calcium per acre soluble in carbonated water, indicating that it was reasonably well supplied with available lime material. On the other hand, due to its very low content of nitrogen and phosphorus, it gave very marked increases for applications of nitrogenous or phosphatic fertilizers.

Several of the fertile soils studied in this work were found to be growing good red clover or alfalfa without the use of lime. These are shown in table 8 and include only soils not given in table 7, because no direct comparisons with limed soil were available and hence it was impossible to say how much these might have been benefitted by the use of liming materials. In should be remembered that practically all the soils shown in table 7 have also produced good yields of clover or alfalfa either where untreated or where fertilized with manure or phosphates. It will be seen in table 8 that the soluble calcium content of these soils is not lower than 760 pounds and in most cases well above this figure. Furthermore, these are all fairly strong soils and most of them have had some special treatment.

TABLE 8

Calcium soluble in .04 N carbonated water and acidity of soils producing good clover or alfalfa without liming

LAB. NO.	LOCATION	SOIL TYPE	SOIL TREATMENT	Ca PER ACRE SOLUBLE IN .04 N H_2CO_3	ACIDITY TRUOG TEST
				lbs.	
310, 311	Marshfield, Wis.	Colby silt loam	Virgin soil	940	3
316, 317	Marshfield, Wis.	Colby silt loam	Manure,	860	3
352, 353	Marshfield, Wis.	Colby silt loam	Manure, rock P.	1030	3
372, 373	Dane, Wis.	Carrington silt loam	Manure, tobacco	760	4 −
324, 325	Junction City, Wis.	Colby silt loam	Manure, bone.	970	2 +
344, 345	Wanakee, Wis.	Carrington silt loam	None	930	3 +
362, 363	Neilsville, Wis.	Auburn loam	Old milk lot, now orchard	2870	None
374, 375	Neilsville, Wis.	Colby silt loam (rolling phase)	Manured, near barn	1080	2 +

While it is not thought possible at the present time and with the limited amount of data, to say that a definite quantity of calcium soluble by this method is necessary for the most profitable growth of crops, there have been found no soils in this work having more than approximately 700 pounds of calcium soluble in 0.04 N carbonated water that have indicated by field tests a serious need for lime. On the other hand, all the soils studied that have been decidedly lower than this amount of soluble calcium have in most cases shown a fairly good return for liming. This point, however, needs further investigation, for it is likely that different classes or types of soils may show marked differences in the necessary calcium supply, especially when the general fertility is considered.

VARIATION IN SOLUBLE CALCIUM CONTENT IN SOILS OF APPROXIMATELY THE SAME ACIDITY

That soils of approximately the same acidity may vary widely in their content of total calcium or calcium soluble in normal and 0.2 N HCl has been shown by Swanson, Latshaw and Tague (22). A similar variation was found in the present work with 0.04 N carbonated water.

The range of variation in the soluble calcium content of different soils or soils having different treatments but showing similar degrees of acidity is given in table 9.

The soils reported in this table include those from widely different types of Wisconsin and Missouri soils. In addition many of the soils had received different soil treatments, such as manure, fertilizer or lime.

Some soils in each group used in this study had as little calcium soluble in 0.04 N carbonated water as approximately 500 pounds an acre. The maximum was much more variable, being 880 pounds in the strongly acid soils and 2920 pounds in one of the peat soils sowing slight acidity and which had

TABLE 9

Variation in the amounts of calcium soluble in .04 N carbonated water in soils having approximately the same degree of acidity

NUMBER OF SOILS ANALYZED	ACIDITY TRUOG TEST	RANGE IN SOLUBLE Ca PER ACRE
		lbs.
11	Strong	494 to 880
19	Medium	510 to 1030
14	Slight	566 to 2920
10	Very slight	500 to 2870

been limed. It should be said, however, that only two unlimed soils showed more than 1150 pounds calcium soluble in 0.04 N carbonated water. One of these was a peat and the other Auburn loam from an old milk lot.

It was found in each group of soils, based on the degree of acidity, that it has been the soils with low amounts of soluble calcium that have shown the greatest need for applications of lime in the field. This fact was previously brought out in the report on the untreated soils shown in tables 6 and 7.

The results obtained on the soils reported in this paper would seem to indicate that, with any degree of acidity, soils having a low amount of calcium soluble in 0.04 N carbonated water may reasonably be expected to give at least favorable results from applications of lime. On the other hand, if a soil has a large supply of soluble calcium it is highly probable that additional applications of liming materials will be only very slightly beneficial and from a practical standpoint the cost may often overbalance the increased returns from the crops. Where the phosphorus content is low and there is a fairly good supply of soluble calcium it is likely that additions of phosphorus will be more beneficial than applications of lime.

EFFECTIVENESS OF CARBONATED WATER AS A SOLVENT

The effect of carbonated water as a solvent is shown by comparing the amount dissolved by this method with the total calcium content of a number of soils. Table 10 shows that as an average of seventeen soils, 9.32 per cent of the total calcium was dissolved by carbonated water, while the per cent soluble ranged from 4.21 in one sample of Carrington silt loam to 37.33 in the Vesper sandy loam. These figures compare very well with Shedd's results (20), as he found from 3.8–10.6 per cent of the total calcium of Kentucky soils soluble in carbonated water.

TABLE 10

Total magnesium and calcium compared with the calcium soluble in .04 N carbonated water

LOCATION (WISCONSIN)	SOIL TYPE	TOTAL Mg*	TOTAL Ca*	Ca SOLUBLE IN .04 N H_2CO_3	Ca SOLUBLE IN 04 N H_2CO_3
		per cent	per cent	per cent	per cent (of total Ca)
Coddington	Peat	0.28	1.715	0.1285	7.48
Morrisonville	Carrington silt loam	0.33	0.83	0.035	4.21
Marshfield	Colby silt loam, virgin	0.41	0.70	0.047	6.71
Marshfield	Colby silt loam, 102A	0.41	0.63	0.0575	9.12
Wanakee	Carrington silt loam	0.52	0.63	0.046	7.30
Marshfield	Colby silt loam (new farm)	0.43	0.62	0.043	6.93
Marshfield	Colby silt loam 202A	0.41	0.61	0.040	6.55
Neilsville	Colby silt loam (rolling)	0.38	0.59	0.0445	7.50
Janesville	Waukesha silt loam (County farm)	0.41	0.57	0.041	7.19
Junction City	Colby silt loam	0.40	0.56	0.0485	8.66
Janesville	Waukesha silt loam (Hughes Farm)	0.47	0.545	0.044	8.07
Hancock	Plainfield sand	0.04	0.545	0.0345	6.33
Dane	Carrington silt loam	0.375	0.525	0.038	7.23
Dane	Carrington silt loam	0.37	0.515	0.035	6.79
Stockton	Plainfield sandy loam	0.21	0.415	0.0355	8.55
Plover	Waukesha sand	0.09	0.205	0.0255	12.43
Neilsville	Vesper fine sandy loam	0.04	0.075	0.028	37.33

* Determinations of total Mg and Ca were made by Mr. M. Tosterud, in the Soils Laboratory of the University of Wisconsin.

That the carbonated water extract will indicate the lime need more accurately than the determination of the total calcium is indicated in a few cases in this table. For instance the Plainfield sand has a rather high amount of calcium, while the soluble calcium is relatively low. Experiments have shown that the soil responds fairly well to lime, particularly with alfalfa. In the case of Colby silt loam at Marshfield, plot 202A has given somewhat better increases for liming than 102A which has a much higher soluble calcium content, but the total amounts of calcium differ by only 0.02 per cent. Acidity tests also show 102A to be somewhat less acid.

SUMMARY

The work reported in this paper has not been in progress long enough, nor has it included a sufficient number of soils to permit drawing definite conclusions, but the principal points studied are as follows:

1. A study was made between the amounts of calcium in different forms in soils and the results obtained in the field from applications of lime. Comparisons were made with the results of ordinary acidity determinations. Determinations were made on the soil solution obtained by the displacement method.

2. In nearly all cases liming increased the amount of calcium in the displaced soil solution. The few instances where this was not the case can probably be explained by the fact that the increased growth of clover had absorbed more of this element from the limed land.

3. The calcium content of the soil solution was reduced 22–54 per cent by the presence of a clover crop on the Colby silt loam.

4. Soils kept in the greenhouse showed great variation in the calcium content of the displaced solution as compared with field samples taken in the spring. The calcium in the soil solution was greatly increased in the strongly acid Colby silt loam when kept under greenhouse conditions for a period of six months.

5. Soils allowed to stand in the greenhouse after the crop was removed showed a rapid increase in the calcium content of the soil solution. This was probably due largely to hydrolysis and to the dissolving action of carbon dioxide in solution as well as by other soil acids.

6. No very definite correlation was found between the calcium in the soil solution and the need for lime in the field. There are so many factors which cause this calcium content to vary, that it changes greatly from season to season.

7. Soils which had given good returns for lime in the field were compared with soils on which the returns for lime had been medium to poor. It was found that the average acidity of the two sets was about the same according to the Truog test. Determinations showed, however, that the calcium soluble in 0.04 N carbonated water averaged only 553 pounds an acre on the soils giving marked increases for lime and 810 pounds an acre on soils giving small returns for applications of liming materials.

8. It was further noted that marked increases due to liming were mainly on infertile soils. That is, they averaged but 1619 pounds nitrogen and 624 pounds phosphorus an acre. The mineral soils giving small returns for lime averaged 3736 pounds nitrogen and 1114 pounds phosphorus per acre. The analysis of the peat soil brought the average considerably above these figures.

9. It would seem from these results that if a soil is well supplied with nitrogen, phosphorus, and a fair amount of calcium soluble in carbonated water, is will likely produce good yields of the common field crops in spite of a considerable amount of soil acidity.

10. In case one of the elements of fertility is greatly lacking and the calcium soluble in carbonated water is reasonably high, as was true on the Clarksville silt loam, the addition of phosphorus or other deficient element may give far greater returns than the application of limestone.

11. Soils of approximately the same acidity may vary widely in their amount of calcium soluble in carbonated water. All the soils studied regardless of treatment were arranged in groups according to their acidity. It was found that soils showing strong acidity varied in their soluble calcium content of 494–880 pounds per acre; those of medium acidity 510–1030 pounds; those of slight acidity 566–2920 pounds; and those of very slight acidity 500–2870 pounds per acre.

12. When the return per ton of limestone was considered it was found to show a closer relation in different soils to the amount of calcium soluble in 0.04 N carbonated water than to the degree of soil acidity. That is, where there was a low amount of soluble calcium there was usually a greater return for liming than where there was already a large amount of calcium present that could be dissolved in this weak acid.

13. The carbonated water extracted on the average 9.32 per cent of the total calcium in the soils studied.

14. Further work is being carried out on this problem to determine more definitely the concentration of carbonated water, the time of extraction, and methods of drying and preparing the samples that will give results showing the best correlation with the effects of soil treatments in the field. Studies are also being made on the calcium content of subsoils and its relation to the conditions to be found in the surface layer.

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CARBON DIOXIDE PRODUCTION OF PLANT ROOTS AS A FACTOR IN THE FEEDING POWER OF PLANTS[1]

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It is well known that plants differ widely in their composition with respect to the essential elements secured from the soil. That this is the case is shown by a compilation of data from a large number of different sources (8). The objection has been made (7) that the results were obtained from plants grown on a number of different soils whose composition and fertility are unknown, and that therefore the differences may not be reliable.

The composition and fertility of the soil undoubtedly have considerable influence on the composition of the plant. However, several workers (6, 7, 9, 14, 16) have shown that when different species of plants are grown on the same soil they differ in composition. These differences are ordinarily attributed to differences in the feeding power of the plants. Undoubtedly the feeding power of a plant is affected by many factors, but the relative importance of these factors is not clearly understood at present.

At one time it was believed that the feeding power of plants was due to the excretion of acids from the plant roots. Later it was shown that carbon dioxide was the only acid excreted in significant quantities and that all plants excrete carbon dioxide from their roots. It has been generally recognized that the carbon dioxide given off by the plant roots would have a solvent effect on the soil minerals, thereby increasing their availability to the plant. The importance of this solvent action is not definitely known, and there is some doubt as to whether or not differences in the feeding power of plants can be attributed to differences in carbon dioxide production. This paper presents some of the results secured in an investigation that is being made to determine (a) whether or not the excretion of carbon dioxide from plant roots is an important factor in the feeding power of plants; and (b) whether or not differences in the feeding power of plants can be attributed to differences in the amount of carbon dioxide excreted from the roots.

A good review of the literature on the importance of the carbon dioxide of the soil air is given by Turpin (13). He also discusses the influence of different factors, including the crop, on the amount of carbon dioxide in the soil air. Therefore, an extensive review of the literature on the subject is unnecessary. Only the more important papers bearing directly upon the problem will be considered.

Stoklasa and Ernest (15) have shown that the amount of phosphorus and potassium absorbed from gneiss and basalt by different plants is proportional to the carbon dioxide produced per gram of dry matter of the roots. Aberson (1) working with young plants concluded that the carbon dioxide excreted by plants was sufficient to bring into solution insoluble soil minerals, especially phosphates. Pfeiffer and Blanck (9) studied the assimilation of phosphorus from soil cultures, fertilized with different phosphates, which were saturated with carbon dioxide three times a week. They found that the carbon dioxide treatment was

favorable when used with soluble phosphates, but with insoluble phosphates it was not beneficial. They also found that lupines and peas absorbed more phosphorus than oats and that the carbon dioxide treatments did not change this relation.

Newton (7) in a study of the absorption of elements by barley and peas found that absorption was practically the same when nutrient solutions were used. When grown in soil cultures the peas absorbed larger amounts of calcium, magnesium, nitrogen and phosphorus. He attributes this difference in absorption in the soil to a difference in the amount of carbon dioxide excreted by the plant roots. Studies on carbon dioxide production in sand cultures showed that the roots of peas gave off approximately twice as much carbon dioxide in a given period of time as did the roots of barley.

Truog (11, 12) does not consider differences in carbon dioxide production as a satisfactory explanation of the differences in the feeding power of plants. He explains differences in the feeding power of plants for calcium, potassium, and phosphorus in rock phosphate on the basis of the law of mass action and chemical equilibrium. The acidity of the plant sap is considered as one of the most important factors affecting the equilibrium and consequently the feeding power of the plant.

Davis, Hoagland and Lipman (5) criticise the theory of Truog. Basing part of their argument on the results of Newton (7), they attribute considerable importance to the extent of the root system and to the excretion of carbon dioxide from the plant roots.

DISCUSSION OF EXPERIMENTAL METHODS

Two general methods have been used in these experiments to study the importance of carbon dioxide production as a factor in the feeding power of plants. In the first method the carbon dioxide production of a number of different plants grown in soil cultures was studied throughout the growing period. As was to be expected, considerable differences in carbon dioxide production were found among the different plants. When the plants reached the blooming stage, they were harvested and analyzed to determine their composition with respect to several of the essential elements. Large and apparently characteristic differences were found in plant composition. The two sets of data were then studied to determine whether or not the differences in composition could be attributed to differences in the amount of carbon dioxide excreted from the plant roots.

The carbon dioxide production of the plant roots was studied in three different ways. (1) The percentage of carbon dioxide in the soil air was determined at frequent intervals, usually twice a week. (2) The amount of carbon dioxide produced in a period of six hours was determined by drawing a definite volume of air through the culture and absorbing the carbon dioxide. This determination was made once each week during the growing period. (3) In one experiment the total amount of carbon dioxide given off during the growing period was determined. Plants were grown in sealed cultures which were aspirated, the carbon dioxide absorbed and measured each day.

In the second general method used in the investigation, the carbon dioxide was removed from the cultures by continuous aspiration. In this manner the carbon dioxide content of the soil air was reduced to 0.20 per cent or less. The aspiration would certainly hasten the removal of carbon dioxide from

around the root hairs and thus reduce the importance of carbon dioxide as a factor determining the amount of the different elements absorbed by the plant. Obviously it is impossible to completely remove carbon dioxide as a factor in this manner. However, rapid, continuous aspiration should reduce its influence and should affect the composition of the plant if carbon dioxide production is a determining factor in the feeding power of plants.

In addition to these methods of studying the problem, use was made of sand cultures. Different plants were grown in sand cultures with nutrient solutions. Absorption was studied by determining the composition of the plants. In such cultures carbon dioxide production should not influence absorption, since all the essential elements are in solution. A difference in composition would therefore indicate that one or more factors other than carbon dioxide production was responsible.for the difference in absorption.

More detailed descriptions of the methods used will be given when the different experiments are considered.

Standard methods of analysis were used in determining the composition of the plant.

EXPERIMENT I

The purpose of this experiment was to determine whether or not there was a correlation between the carbon dioxide production of different plants and their feeding power. Carbon dioxide production was measured by determining the percentage of carbon dioxide in the soil air at intervals during the growing period. The feeding power of the plant is indicated by its composition with respect to the various elements.

Velvet beans, buckwheat, sorghum, cowpeas and soybeans were grown in two gallon soil cultures. The soil was a slightly acid sandy loam of medium fertility, nitrogen being the element limiting the growth of non-leguminous crops. Nitrate of soda was applied to the buckwheat and sorghum cultures as soon as it became evident that a lack of nitrates was limiting their growth. The buckwheat received one gram of $NaNO_3$ twenty-seven days after planting. The sorghum received one gram twenty-seven days after planting and another gram twenty days later. All cultures were watered with distilled water.

The plants were grown until they were in bloom except in the case of velvet beans. The latter made an excellent growth, but did not bloom. There were four plants in each two gallon culture except in the case of buckwheat where there were eight plants per culture. All cultures were in duplicate and the figures given for composition and carbon dioxide production are the averages.

The carbon dioxide content of the soil air was determined by the following procedure:

The 2-gallon glazed earthenware culture vessels were provided with a drainage hole near the bottom. A piece of glass tubing extended from the center of the jar near the bottom, through a paraffined cork stopper, to the outside. A sample of the soil air could readily be obtained by drawing it out through this tube. To obtain and analyze a uniform sample, a definite amount of $0.1N$ $Ba(OH)_2$ was introduced into a 500-cc. filter flask. Immediately after the introduction of the $Ba(OH)_2$, the flask was stoppered and connected with a strong filter pump for two minutes. This almost completely evacuated the flask. A stopcock on the side tube was closed, and the flask connected with the glass tube extending into the soil culture. Upon opening the stopcock the soil air was drawn into the flask. The stopcock was

then closed, the flask shaken to absorb all carbon dioxide and the excess of Ba(OH)₂ was titrated with HCl. The temperature and barometric pressure were determined and the proper correction applied.

This method of sampling and analyzing the soil air is accurate and rapid. The results are easily duplicated if the proper precautions are used. It is essential that the evacuation should be uniform so that all samples are of the same size. Frequent determinations of the degree of evacuation and size of sample are necessary to insure uniformity. It is necessary to have the moisture content of the culture uniform. If the culture dries out somewhat, the carbon dioxide will diffuse out more readily and much lower results will be secured than in the case of a similar culture with a higher moisture content.

Experimental results have been secured which show that carbon dioxide production is greater at certain times of the day than at others, the maximum production being in the early part of the afternoon. Accordingly all determinations of the carbon dioxide content of the soil air should be made at the same time of day. This was done in experiment 2. In experiment 1, some

TABLE 1

Carbon dioxide content of the soil air under different crops

AGE OF PLANTS	NUMBER OF DETERMINATIONS IN PERIOD	VELVET BEANS	BUCKWHEAT	SORGHUM	COWPEAS	SOYBEANS	NO CROP
days		*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
1–14	2	0.19	0.17	0.19	0.19	0.17	0.19
15–28	4	0.80	0.40	0.67	0.99	0.54	0.19
29–42	4	2.51	1.08*	2.03	2.28	1.78	0.21
43–56	3	2.74	....	1.27	2.83	2.11	0.18
57–70	3	2.74	....	2.49	2.91*	1.69	0.16
Maximum percentage.		3.94	1.58	3.30	4.32	2.70	0.24

* Average of two determinations.

of the determinations were made in the morning, and others in the afternoon. However, the determinations on all cultures for a given day were made at approximately the same time so the results are comparable.

The results for carbon dioxide production are shown in table 1. All crops caused a large increase in the carbon dioxide content of the soil air. The greatest increase was caused by cowpeas and velvet beans. The smallest increase and therefore the smallest excretion of carbon dioxide from the plant roots was found in the buckwheat cultures. Sorghum and soybeans produced about the same increase, the former causing a slightly greater increase in the carbon dioxide content of the soil air.

Table 2 gives the age, yield and analysis of the different crops. The analysis is given on the percentage basis which is considered preferable to calculating the total amount of the different elements removed by the crop. The latter may be calculated from the table and will be considered in the discussion of the results.

The data in table 2 make possible some very interesting comparisons between the different crops. Sorghum and cowpeas were harvested at almost the same time. The dry weights are identical and yet their analyses are widely different. The cowpeas had an ash content more than double that of the sorghum, the calcium content was 364 per cent greater, the magnesium content approximately double, and the nitrogen content 261 per cent greater than that of sorghum. Evidently there is a great difference in the feeding power of the two plants. A study of the results for carbon dioxide production shows that the plants are not widely different in this respect. Cowpeas at all times produced a slightly higher percentage of carbon dioxide in the soil air than did sorghum. It does not seem probable that this difference in carbon dioxide production is great enough to account for their difference in feeding power.

Buckwheat and sorghum also afford an interesting comparison of crops with radically different feeding powers. Sorghum had a growing period twice as long as did the buckwheat. It produced twice as much dry weight. However, analysis shows that the ash content of the buckwheat was 309 per

TABLE 2

The yield and percentage (dry weight) composition of different crops grown in soil cultures

CROP	AGE AT HARVEST	WEIGHT OF DRY TOPS	ASH	Ca	Mg	P	N
	days	*gm.*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Velvet beans...........	96	42.15	4.63	1.07	0.29	0.11	1.54
Buckwheat............	35	6.12	11.55	1.86	0.54	0.44	2.29
Sorghum.............	68	12.25	3.73	0.39	0.21	0.18	1.08
Cowpeas.............	64	12.17	8.77	1.42	0.39	0.22	2.82
Soybeans.............	88	22.50	4.45	0.71	0.33	0.16	2.06

cent higher, the calcium content 476 per cent higher, the magnesium content 257 per cent higher, the phosphorus content 244 per cent higher and the nitrogen content 212 per cent greater than that of sorghum. If the total amount of the different constituents taken up by the plants is calculated, it will be found that in every case buckwheat absorbed more than did sorghum. The percentage increase in total amount absorbed is obtained by subtracting 200 from the figures given above.

That this great difference in the feeding power of the two plants is not due to a difference in carbon dioxide production is evident from a study of table 1. Buckwheat has a very limited root system and carbon dioxide production is very limited. Sorghum has a very extensive root system and produces considerable quantities of carbon dioxide. The difference in the feeding power of the two crops cannot be attributed to differences in the extent of the root system or to differences in carbon dioxide production. It must be due to some other factor or group of factors. The high acidity of the buckwheat sap (12) may be a partial explanation of the difference.

Soybeans and sorghum were similar in carbon dioxide production as indicated in table 1. Soybeans had a considerably higher percentage of ash, calcium, magnesium and nitrogen. A comparison of the total amount of the different elements absorbed shows that the soybeans absorbed very much larger amounts of all elements than did the sorghum. Sorghum produced slightly larger amounts of carbon dioxide and consequently it is impossible to explain the results on the basis of differences in carbon dioxide production.

Further comparisons might be made from the results set forth in tables 1 and 2. However, in no case is there good evidence that differences in the feeding power of the plants can be attributed to differences in carbon dioxide production from the plant roots.

EXPERIMENT 2

One object of this experiment was a verification of the results secured in the preceding experiment. A second object was to determine what effect removing carbon dioxide from the culture would have on the feeding power of the plant as indicated by its composition.

The cultures were grown in two series. Series 1 was not aspirated and the carbon dioxide content of the soil air was determined twice a week. Series 2 received rapid, continuous aspiration during the entire growing period. All cultures were in 4-gallon glazed earthenware jars provided with a glass tube near the bottom as described in experiment 1. The soil was a rather poor, slightly acid Norfolk sandy loam from the experiment station farm. The crops and fertilizer treatment are indicated in table 3. Sodium nitrate was applied at the rate of three grams per culture at the time of planting. The cowpeas and soybeans were grown with and without the application of the nitrate. This seemed desirable as the fertilization might influence the composition to a considerable extent. All cultures were in duplicate, with five plants per culture except with buckwheat which had ten plants and cotton which had three plants per culture.

Table 3 shows the carbon dioxide content of the soil air in series 1 during successive 7-day periods. Figure 1 shows the same results except that the individual determinations are plotted instead of the average for the week. The results for the cowpeas and soybeans which did not receive sodium nitrate are not shown in figure 1. The fertilization of these crops caused a greater and more rapid growth and increased carbon dioxide production.

The results show that cowpeas excrete more carbon dioxide than any of the other crops. Soybeans, sorghum and cotton are similar with respect to their influence on the carbon dioxide content of the soil air. As in experiment 1, soybeans and sorghum gave nearly the same result. Cotton, a plant which will make a satisfactory growth on poorer soils than will soybeans or sorghum, produced less carbon dioxide than either of the latter. Buckwheat roots gave off very little carbon dioxide. These results agree very well with those secured in experiment 1, the chief difference being that the cowpeas in experiment 2 evidently gave off more carbon dioxide than the cowpeas in experiment 1. This difference is not great when the com-

parison is made with the cowpea cultures which did not receive sodium nitrate.

The carbon dioxide production of these crops was also measured by the aspiration method. In this method the cultures of series 2 receiving continuous aspiration were used. The cultures were aspirated at the rate of 6000 cc. per hour for six hours. The air from the culture was drawn through a Truog carbon dioxide absorption apparatus (10) where the carbon dioxide

TABLE 3

*Carbon dioxide content of the soil air under different crops**

AGE OF PLANTS	SORGHUM	COWPEAS	BUCK-WHEAT	SOYBEANS	COTTON	COWPEAS NO NaNO₃	SOYBEANS NO NaNO₄	NO CROP
days	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
15–21	0.79	1.26	0.82	0.88	0.84	1.14	0.86	0.65
22–28	0.86	1.83	0.84	1.15	1.01	1.67	0.91	0.46
29–35	1.26	3.20	0.79	1.40	1.25	2.39	1.14	0.39
36–42	1.68	5.11	....	2.34	1.85	3.71	1.20	0.25
43–49	1.60	3.27	....	1.76	1.38	2.58	0.96 ·	0.14
50–56	2.59	3.43	....	2.20	1.85	3.20	1.70	0.20
57–63	2.51	2.69	....	2.04	1.85	2.78	1.95	0.13

* Figures are the average of duplicate determinations made on two different days.

TABLE 4

Carbon dioxide obtained from soil cultures of different crops by the aspiration method

AGE OF PLANTS	SORGHUM	COWPEAS	BUCK-WHEAT	SOYBEANS	COTTON	COWPEAS NO NaNO₃	SOYBEANS NO NaNO₄	NO CROP
days	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*
16	0.09	0.14	0.12	0.12	0.10	0.15	0.12	0.09
23	0.13	0.22	0.16	0.17	0.14	0.25	0.19	0.07
30	0.17	0.45	0.13	0.24	0.24	0.38	0.22	0.07
37	0.21	0.48	....	0.26	0.21	0.39	0.16	0.06
44	0.16	0.36	....	0.17	0.17	0.26	0.15	0.04
51	0.24	0.42	....	0.24	0.17	0.32	0.22	0.04
58	0.28	0.39	....	0.22	0.18	0.37	0.28	0.04
Total......	1.28	2.46	0.41	1.42	1.21	2.12	1.34	0.41
Average....	0.18	0.35	0.14	0.21	0.17	0.30	0.20	0.06

was absorbed in 0.4 N Ba(OH)₂. When aspiration was stopped the excess Ba(OH)₂ was titrated with HCl and the grams of carbon dioxide obtained from the culture were calculated. The determinations were made weekly and the results shown in table 4 are for single determinations. This method gives results very similar to those obtained by the sample method, shown in table 3. Cowpea roots give off the most carbon dioxide. Soybeans, sorghum and cotton rank in the order named, but the differences between them are small. Buckwheat ranks far below the other crops in carbon dioxide production.

The buckwheat was harvested thirty-five days after planting, when it was in full bloom. All other crops were harvested at the end of sixty days as they were all in bloom, except cotton. The cotton had made a good growth and had from two to three squares per plant. Table 5 gives the age, dry weight and analysis of the crops from the non-aspirated cultures, series 1.

Cotton and sorghum were similar in carbon dioxide production but sorghum undoubtedly has a more extensive root system than cotton which is a tap-
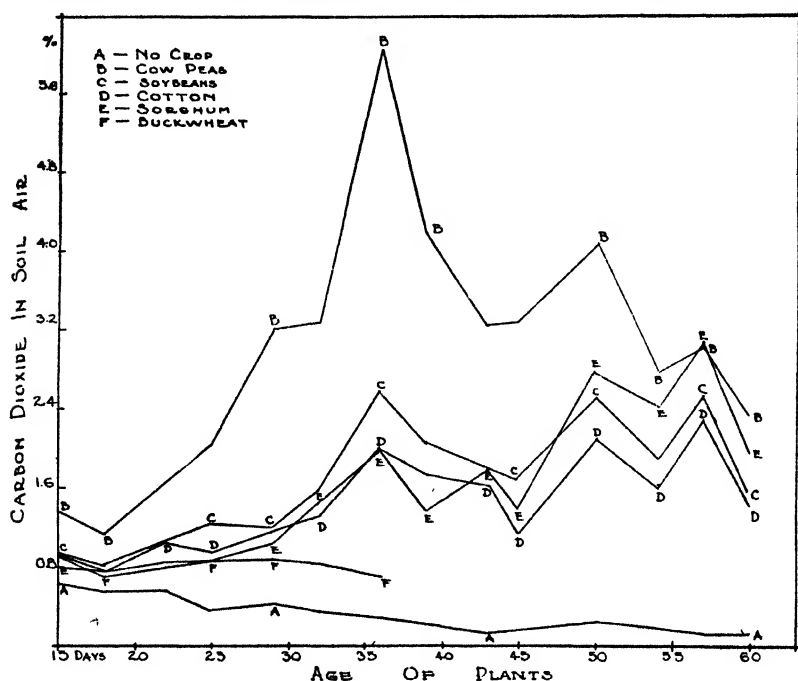
FIG. 1. PERCENTAGE OF CARBON DIOXIDE IN THE SOIL AIR OF CULTURES OF DIFFERENT PLANTS

rooted plant. From a consideration of those two factors one would conclude that sorghum would have the greater feeding power. The analysis shows, however, that the cotton plant has more than double the ash content of sorghum. The calcium content is practically four times as great and the magnesium, potassium, phosphorus and nitrogen content of the cotton is considerably higher than that of sorghum.

If the comparison is made on the basis of the total amount absorbed the relation is not changed materially. It is evident therefore that the difference in feeding power cannot be attributed to differences in carbon dioxide production or extent of the root system.

The sorghum and the soybeans receiving nitrate of soda produced nearly the same amount of carbon dioxide and their dry weights are almost identical. The soybeans contained a higher percentage of all elements for which analysis was made. The difference was greatest in the case of the percentage of ash, calcium and nitrogen.

Buckwheat, with a small root system and producing a small amount of carbon dioxide, contained a much higher percentage of all constituents than did sorghum. Considering the amounts absorbed there would be very little difference between the two plants. It seems probable that the high feeding power of buckwheat may be due to the high acidity of its cell sap as suggested by Truog (12). It should be noted, however, that the buckwheat contained a very high percentage of potassium, more than double that of any other crop except cotton. The buckwheat in its short growing period, and making

TABLE 5

The yield and percentage (dry weight) composition of different crops grown in four gallon soil cultures

CROP	AGE AT HARVEST	WEIGHT OF DRY TOPS	ASH	Ca	Mg	K	P	N
	days	gm.	per cent	per cent	per cent	per cent	per cent	per cent
Sorghum.....	60	28.45	3.85	0.53	0.36	0.88	0.12	1.46
Cotton.......	60	20.20	9.14	2.00	0.49	1.22	0.21	2.20
Buckwheat...	35	12.20	8.76	1.00	0.79	2.33	0.12	2.36
Cowpeas.....	60	40.40	6.01	1.24	0.39	0.89	0.12	2.39
Soybeans.....	60	27.60	6.43	1.40	0.45	1.03	0.16	2.19
Cowpeas*....	60	25.50	6.45	1.34	0.43	0.92	0.13	2.37
Soybeans*....	60	22.75	6.47	1.31	0.39	1.12	0.16	2.47

* Were not fertilized with $NaNO_3$.

a small dry weight, took up more potassium than any other culture except the cowpeas which received sodium nitrate. This result is in apparent disagreement with the statement of Truog (12) that buckwheat is a poor feeder on mineral potash. Additional experimental evidence must be secured to determine the potassium requirement of buckwheat, and to determine its feeding power for potassium as compared to that of other plants.

·The greatest production of carbon dioxide was in the cowpea cultures fertilized with nitrate. These plants contained a smaller percentage of all mineral constituents than did cotton or soybeans receiving the same fertilization. However, due to the fact that they made a greater growth, the fertilized cowpeas absorbed a larger amount of the different elements than did any other culture. This is in accordance with the amount of carbon dioxide produced. However, if comparison is made with sorghum or soybeans the increase in the amount of the different elements absorbed is not proportional to the increase in carbon dioxide production.

Fertilization with sodium nitrate increased the dry weight and carbon dioxide production of cowpeas and soybeans, but it did not have an appreciable effect on the percentage composition of the plants. Even the nitrogen content was not increased.

The results of this experiment serve to verify those obtained in the first experiment. In neither case was evidence obtained which would indicate that the carbon dioxide production of plant roots was associated with the feeding power of the plants.

THE INFLUENCE OF CONTINUOUS ASPIRATION ON THE FEEDING POWER OF THE PLANT AS INDICATED BY ITS COMPOSITION

As has been indicated, the cultures in series 2 were identical in all respects to those for which data have just been given, except that they received continuous aspiration, the purpose being to remove carbon dioxide as a factor influencing the feeding power of the plant. Aspiration was continuous throughout the growing period. The average rate of aspiration was approximately twenty-five to thirty liters per hour. This was produced by connecting all the cultures with a strong filter pump. Several times during the growing period the carbon dioxide content of the soil air was determined. The maximum percentage found in any culture was 0.24 per cent. The average of all determinations was 0.16 per cent. As has been shown in table 3 the carbon dioxide content of the air in the non-aspirated cultures was seldom less than 1.50 per cent, and was frequently as high as 2.00 or 3.50 per cent. Therefore, the method was effective in removing most of the carbon dioxide from the culture.

There are certain objections to the method. The thorough aeration would increase bacterial activities such as nitrification. This is not considered a serious objection as aeration in the sandy soil was very good in the non-aspirated cultures. Also the application of three grams of sodium nitrate per culture would tent to prevent increased nitrification from influencing growth and absorption of the plant.

The most serious objection is that the carbon dioxide was not completely removed. The root surfaces are in such intimate contact with the soil particles that the solvent action of the carbon dioxide would take place before the removal of the carbon dioxide. This is undoubtedly true to a certain extent. Nevertheless the rapid aspiration would certainly hasten diffusion from these surfaces and reduce the solvent action of the carbon dioxide. It would be difficult to determine the effectiveness of the removal from the root surfaces. The writer is of the opinion that the removal is effective enough to influence the composition of the plant if carbon dioxide production is an important factor in the feeding power of plants. Cotton and cowpeas have a high feeding power for calcium. If this is due to the carbon dioxide given off by the plant roots it seems probable that the plants in the aspirated cul-

tures of series 2 would contain a smaller percentage of calcium than those in the non-aspirated cultures of series 1.

TABLE 6

The yield and percentage (dry weight) composition of plants grown in soil cultures with and without the removal of carbon dioxide by continuous aspiration

TREATMENT	SORGHUM	COTTON	BUCK-WHEAT	COWPEAS	SOYBEANS	COWPEAS*	SOYBEANS*
Dry weight of tops							
	gm.	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*
CO₂ not removed	28.45	20.20	12.20	40.40	27.60	25.50†	22.75
CO₂ removed	23.15	20.90	12.50	37.55	28.70	33.65	19.15
Difference	−5.30	0.70	0.30	−2.85	1.10	8.15	−3.60
Ash Content							
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
CO₂ not removed	3.85	9.14	8.76	6.01	6.43	6.45	6.47
CO₂ removed	3.98	7.96	9.48	5.49	5.51	6.19	6.71
Difference	0.13	−1.18	0.72	−0.52	−0.92	−0.26	0.24
Calcium Content							
CO₂ not removed	0.53	2.00	1.00	1.24	1.40	1.34	1.31
CO₂ removed	0.57	1.81	1.22	1.16	1.16	1.49	1.43
Difference	0.04	−0.19	0.22.	−0.08	−0.24	0.15	0.12
Magnesium Content							
CO₂ not removed	0.36	0.49	0.79	0.39	0.45	0.43	0.39
CO₂ removed	0.36	0.46	0.83	0.37	0.39	0.40	0.45
Difference	0.00	−0.03	0.04	−0.02	−0.06	−0.03	0.06
Potassium Content							
CO₂ not removed	0.88	1.22	2.33	0.90	1.03	0.92	1.12
CO₂ removed	0.93	1.13	2.29	0.83	0.97	0.82	1.19
Difference	0.05	−0.09	−0.04	−0.07	−0.06	−0.10	0.07
Phosphorus Content							
CO₂ not removed	0.12	0.21	0.12	0.12	0.16	0.13	0.16
CO₂ removed	0.13	0.20	0.13	0.10	0.15	0.12	0.18
Difference	0.01	−0.01	0.01	−0.02	−0.01	−0.01	0.02
Nitrogen Content							
CO₂ not removed	1.46	2.20	2.36	2.39	2.19	2.37	2.47
CO₂ removed	1.65	2.75	2.37	2.13	1.69	2.15	2.28
Difference	0.19	0.55	0.01	−0.26	−0.50	−0.22	−0.19

* Did not receive NaNO₃.

† Poor duplication in this culture, 19.8 and 31.2 gms.

Table 6 shows the effect of aspiration on the yield and percentage composition of the different plants. Taken as a whole the results show that aspiration

had very little influence on either the yield or the composition of the crop. There is no evidence that aspiration had a tendency to make all plants have the same composition as would be the case if aspiration removed carbon dioxide and carbon dioxide was the determining factor in the feeding power of plants. The differences in composition are small and probably are not due to the influence of aspiration. In most cases the differences do not merit serious consideration. However, the results given in the table will be discussed to show certain differences that were obtained.

With four of the seven crops the yield in the aspirated cultures was less than in the non-aspirated cultures. With three of the seven crops the plants from the non-aspirated cultures contained a higher percentage of ash, phosphorus and nitrogen than did the plants from the aspirated cultures. This was the case in two instances with magnesium and potassium and in four instances with calcium. In most cases the differences were small and the results would be considered satisfactory duplicates. For example, the maximum difference found in the percentage of magnesium, phosphorus and potassium was only 0.10 per cent. It is evident that aspiration had almost no influence on the composition of the plants.

Considering the effect upon the composition of individual crops it will be seen that with sorghum the percentage of all constituents was greater in the aspirated cultures than in the non-aspirated cultures. With one exception in each case, this was true of all constituents in buckwheat and in the soybeans which did not receive nitrate. The opposite effect is found in the other cultures. Cotton, both cowpea cultures, and the soybean receiving nitrate had a lower percentage of the different constituents in the aspirated cultures. The differences are small in most instances but they are consistent. It seems impossible to attribute the results to the removal of carbon dioxide. Sorghum and cotton produced similar amounts of carbon dioxide but aspiration apparently increased the percentage of all constituents in one and decreased the percentage in another. Opposite results were also secured with fertilized and unfertilized soybeans. These apparently conflicting results lead to one of two conclusions. Either the excretion of carbon dioxide by plant roots is an unimportant factor in the feeding power of plants, or aspiration is not an effective method of reducing the influence of carbon dioxide production on the feeding power of plants. The author considers the first conclusion correct, especially since the preceding experiments on the relation of carbon dioxide production to the feeding power lead to the same conclusions.

EXPERIMENT 3

In the preceding experiments the excretion of carbon dioxide was studied by observing the percentage in the soil air. The purpose of the third experiment was to determine the total amount of carbon dioxide given off by different plants during the growing period and then to determine the total amount of the various elements absorbed by the plants. By this method

it is possible to determine whether the ratio between the amount of carbon dioxide excreted from the roots and the amount of any element absorbed by the plant is the same or different for different plants.

Cowpeas, buckwheat, sorghum and soybeans were grown in 1-gallon glazed earthenware jars. Seven days after planting, as soon as there were good seedlings, the cultures were sealed with an air tight wax seal. Two days later, after it was evident that none of the plants were injured in applying the wax, the plants were thinned. Four cowpea, soybean and sorghum plants, and eight buckwheat plants were grown in a culture. Cultures were in duplicate
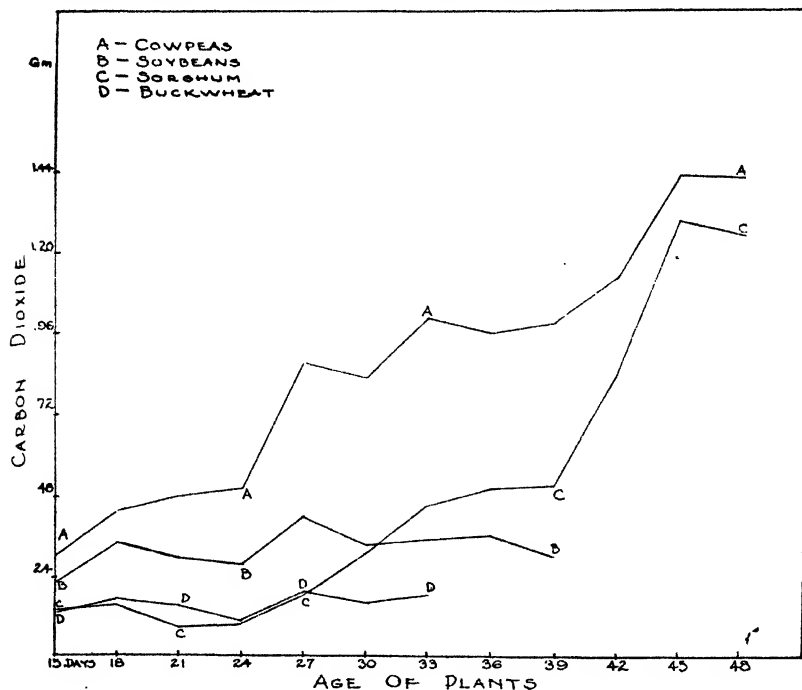
FIG. 2. GRAMS OF CARBON DIOXIDE GIVEN OFF BY THE ROOTS OF DIFFERENT PLANTS DURING SUCCESSIVE 3-DAY PERIODS

and two cultures were carried without a crop. Carbon dioxide determinations were made daily, beginning fourteen days after planting. These determinations were made by aspirating and absorbing the carbon dioxide. The incoming air was freed of carbon dioxide by drawing it through a soda-lime tube. It then passed through a U-tube containing a small amount of water. The cultures were watered through this U-tube, and it served as an indicator as to whether or not the wax seal was perfectly air tight. If bubbling in the U-tube and in the absorption tower was not at the same rate, it indicated a leak in the wax seal. Very little difficulty was experienced in this respect. After passing through the U-tube, the incoming air entered the culture through an inverted two-inch funnel. The large end of the funnel was about two inches below the wax seal. After passing through the soil mass, the air was drawn out at the bottom of the culture and passed through a Truog carbon dioxide absorption

apparatus, containing a measured quantity of 0.4 N Ba(OH)$_2$. Aspiration was continuous during most of the day, but was stopped during the night. The carbon dioxide absorption apparatus was disconnected and the excess Ba(OH)$_2$ titrated every day.

The results for carbon dioxide production are shown in table 7. The figures are given for successive three day periods rather than the results of the daily determinations.

The carbon dioxide production of the different plants is obtained by subtracting the results for the no-crop cultures from the results for the other cultures. These figures are shown graphically in figure 2. The results are similar to those secured in the preceding experiments. Buckwheat roots give off very little carbon dioxide. Cowpeas give off large amounts. Soy-

TABLE 7

Total carbon dioxide secured from soil cultures of different crops during successive 3-day periods

AGE OF CROP	COWPEAS	BUCKWHEAT	SOYBEANS	SORGHUM	NO CROP
days	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*
14–16	0.71	0.54	0.63	0.54	0.40
17–19	0.87	0.61	0.78	0.59	0.43
20–22	0.99	0.66	0.81	0.60	0.51
23–25	1.12	0.73	0.90	0.72	0.62
26–28	1.41	0.75	0.96	0.74	0.54
29–31	1.28	0.61	0.78	0.76	0.45
32–34	1.44	0.62	0.79	0.88	0.43
35–37	1.32	....	0.72	0.86	0.36
38–40	1.34	....	0.64	0.86	0.35
41–43	1.52	....	....	1.22	0.39
44–46	1.84	....	....	1.70	0.40
47–49	1.84	....	....	1.67	0.41
Total....................	15.68	4.51	7.00	11.13	5.28
Increase over no crop.......	10.40	1.12	2.91	5.85	

beans and sorghum show greater differences here than in the preceding experiments. During the early part of the growing period soybeans produced more carbon dioxide than sorghum. This was also the case in experiment 2. (See figure 1). After thirty days the sorghum began to produce much larger amounts of carbon dioxide, and at the time of harvesting it was giving off almost as much as the cowpeas. The sorghum was making a very rapid growth at this time. In general the carbon dioxide production was proportional to the rate of growth.

The yield and composition of the different crops are given in table 8. The results are similar to those secured in the preceding experiments. Table 9 shows the milligrams of the different constituents absorbed by the plant for each gram of carbon dioxide excreted from the plant roots. If the amount of carbon dioxide produced determines the amount of an element absorbed all plants should give similar results. That is, for each gram of carbon dioxide

given off sorghum, buckwheat and cowpeas would take up the same amount of calcium or magnesium. The results show that this is not the case. Widely different results were secured for the different plants. For each gram of carbon dioxide given off by the plant roots, buckwheat took up eight times as much calcium as did sorghum, and more than three times as much as did cowpeas. Buckwheat also took up seven times as much magnesium and four times as much phosphorus per gram of carbon dioxide excreted as did cowpeas or sorghum. Similar comparisons may be made between soybeans and sorghum, soybeans and buckwheat, soybeans and cowpeas, and sorghum and cowpeas. In none of these cases is there much evidence that there is any relation between the amount of carbon dioxide produced and the amount of any element absorbed. Thus this experiment furnishes additional evidence that there is no relation between the carbon dioxide production of a crop and its feeding power.

TABLE 8

The yield and percentage (dry weight) composition of different crops grown in sealed soil cultures

CROP	AGE AT HARVEST	WEIGHT OF TOPS	ASH	Ca	Mg	P̊	N
	days	*gm.*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Cowpeas.............	49	11.37	5.16	1.16	0.39	0.10	2.19
Buckwheat...........	34	3.83	9.70	1.22	0.83	0.14	2.52
Soybeans.............	40	4.40	6.28	1.40	0.47	0.16	3.41
Sorghum.............	49	5.86	4.20	0.50	0.42	0.11	1.70

TABLE 9

Amount of the different elements absorbed by different crops per gram of carbon dioxide given off by the plant roots

CROP	MILLIGRAMS ABSORBED PER GRAM OF CO₂ GIVEN OFF BY THE ROOTS				
	Ash	Calcium	Magnesium	Phosphorus	Nitrogen
Cowpeas..........	56.4	12.7	4.28	1.06	24.0
Buckwheat........	331.1	41.5	28.16	4.81	86.0
Soybeans..........	94.9	21.2	7.07	2.44	51.5
Sorghum..........	42.1	5.0	4.21	1.09	17.0

THE COMPOSITION OF DIFFERENT CROPS GROWN IN QUARTZ SAND CULTURES

In soil cultures the excretion of carbon dioxide has been considered a factor in the feeding power of plants because it is well known that water containing carbon dioxide has a much greater solvent effect on many soil minerals than water free of carbon dioxide. If, as in quartz cultures, the essential elements are supplied in solution the excretion of carbon dioxide should not be a factor in the feeding power of plants. Therefore, if different plants are grown in sand cultures and receive the same nutrient solution they would have the

same composition unless other factors than carbon dioxide production influenced the amount of the different elements absorbed. If the differences found in the composition of the crops grown in nutrient solution are similar to the differences found in the same crops grown in soil cultures it would indicate that the same factors were determining the feeding power in both instances and that carbon dioxide production was not the determining factor in either case.

The composition of different crops grown in sand cultures has been determined by several investigators. Bauer (2, p. 35) determined the percentage of calcium and phosphorus in nine different crops grown in sand cultures with the calcium and phosphorus supplied in soluble and insoluble forms, acid phosphate and rock phosphate. He found that when calcium and phosphorus were furnished as acid phosphate, there were large differences in the calcium and phosphorus content of the different plants. Four leguminous

TABLE 10

Composition of nutrient solution

Ca	NO$_2$	Mg	SO$_4$	K	PO$_4$	Na	Cl	TOTAL
p.p.m.	*p.pm.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*
31	186	51	200	203	175	34	119	996

TABLE 11

The yield and percentage (dry weight) composition of different crops grown in sand cultures

CROP	WEIGHT OF DRY TOPS	ASH	Ca	Mg	K	P	N
	gm.	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Velvet beans..........	15.55	10.2	0.61	0.57	3.49	0.53	2.09
Cowpeas.............	17.53	15.2	0.66	0.85	4.80	0.53	1.45
Sorghum.............	23.67	8.8	0.21	0.41	3.63	0.46	0.95

plants had an average calcium content of 1.23 per cent. All of them contained over one per cent calcium. Corn, timothy and redtop had calcium contents of 0.57 per cent, 0.36 per cent and 0.63 per cent, respectively. Very similar differences were found in the calcium content of these plants when rock phosphate was the source of calcium and phosphorus. These differences in the calcium content of the plants are very similar to the differences found when the plants were grown in soil (8).

Bryan (3, 4) grew oats, wheat, alfalfa, red clover and alsike clover in Cone's nutrient solution at different reactions and determined the calcium content of the plants. The same nutrient solution was used for all cultures except that the legumes did not receive nitrate while the non-legumes received nitrate as KNO$_3$. For the legumes an equal weight of KCl was substituted for the KNO$_3$, and the plants were inoculated. At pH 7 both the oats and wheat had a calcium content of 0.37 per cent. At the same reaction, alfalfa,

alsike clover and red clover had a calcium content of 0.88 per cent, 0.81 per cent and 0.76 per cent, respectively.

Newton (7) grew barley and peas in a nutrient solution and found they had practically the same composition. Similar results were secured with barley and vetch, but beans were found to have a much higher calcium content than barley when grown in the same nutrient solution.

In order to obtain additional data on the composition of different plants grown in nutrient solutions, the writer grew velvet beans, cowpeas, and sorghum in two-gallon sand cultures. Table 10 shows the composition of the nutrient solution used in these cultures. The nutrient solution was renewed twice a week. The five plants in each culture were harvested thirty-six days after planting. Table 11 shows the dry weight and composition of the different plants.

The composition of the legumes and the sorghum differs widely. Sorghum has a lower ash content than either velvet beans or cowpeas. Its calcium content is only one-third as great as that of the legumes. The latter have a higher magnesium, phosphorus and nitrogen content. The differences are of the same order as found when these plants were grown in soil cultures, table 2. Therefore, it may be concluded that factors, other than the excretion of carbon dioxide from the roots, determine the feeding power of plants.

SUMMARY

Four experiments are reported in which a study was made of the relation between the carbon dioxide production of plant roots and the feeding power of the plant. In experiments 1 and 2 carbon dioxide production was studied by determining the influence of the crop on the carbon dioxide content of the soil air at intervals during the growing period. The feeding power of the plants was studied by determining the composition of the plants and also by considering the total amount of the different elements absorbed.

In the second experiment a study was made of the effect of continuous aspiration of the cultures on the feeding power of the plants as indicated by their composition. Aspiration was continuous during the growing period and was at the rate of about twenty-five liters per hour. In this manner the carbon dioxide content of the air was reduced to 0.20 per cent or less.

The total amount of carbon dioxide excreted from the plant roots was determined in the third experiment. After determining the amount of absorption, the amount of the different elements absorbed per gram of carbon dioxide excreted was calculated for sorghum, cowpeas, buckwheat and soybeans.

In the last experiment absorption from a nutrient solution was determined.

A summary of the results obtained in these experiments follows:

1. More carbon dioxide is excreted from the roots of cowpeas than from the roots of any other plant used in the experiments.

2. Buckwheat roots give off very little carbon dioxide.

3. Sorghum, soybeans and cotton are very similar in carbon dioxide production. They produce much more carbon dioxide than buckwheat.

4. Buckwheat has the greatest feeding power of any of the plants used in the experiments. Cotton ranks second in feeding power and sorghum has the lowest feeding power of all the plants used.

5. No relation was found between carbon dioxide production and the feeding power of the plants for calcium, magnesium, phosphorus or potassium in a rather poor sandy soil.

6. The removal of carbon dioxide by continuous, rapid aspiration did not influence the composition of the plants.

7. Different plants absorb widely different amounts of calcium, magnesium and phosphorus per gram of carbon dioxide excreted from the plant roots. For each gram of carbon dioxide excreted by the roots, buckwheat absorbed 41.5 mgm. of calcium; sorghum, cowpeas and soybeans absorbed 5.0, 12.7, and 21.2 mgm., respectively.

8. Cowpeas, velvet beans and sorghum grown in sand cultures absorbed different amounts of calcium, magnesium and nitrogen. The legumes contained much higher percentages of these elements than did the sorghum.

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THE LOSS OF CALCIUM CARBONATE IN DRAINAGE WATER AS AFFECTED BY DIFFERENT CHEMICAL FERTILIZERS[1]

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During the study of problems relating to the use of sulfate of ammonia at this station, numerous data have been accumulated by the analysis of the drainage-waters from the plots used in the fertilizer experiments. When these results were collated and compared, it was noted that the differences in composition of the waters from the various plots were consistent throughout the several years and seasons in which the samples had been collected and analyzed.

The field containing the fertilizer plots has been frequently described (2, 3, 4) under the designation "Field A." It is nearly level, with but a slight slope toward the east and is divided into plots of 0.1 acre each, which are separated from one another by strips of land 5 feet wide. Each plot is 8 rods long and 2 rods wide. Lengthwise of the middle of each plot runs a drain of 2-inch tile at the depth of 3 feet, and its outlet is at the eastern end in a well 2 feet in diameter and 4 feet in depth. A main drain of 6-inch tile runs along the eastern border of the field at a depth of 4 feet and drains the wells.

The surface soil of the field is quite uniform and has been classified as Merrimac sandy loam (10). The mixture of chemicals for each plot has always been applied uniformly over its surface and none has been applied to the strips between the plots. It has been assumed that no cross percolation from plot to plot takes place, as the growing crops show a sharp boundary between the fertilized and unfertilized areas.

During the periods in which the drainage-waters were analyzed, the applications of lime were made upon all the plots, but upon only one-half of each area. The water from each drain however must represent the whole surface of the plot, therefore the concentration of lime in the drainage-waters is necessarily less than it would have been if the application of lime had been made to the entire plot. Hydrated lime was applied in 1909 at the rate of 2.5 tons per acre and in 1913 at the rate of 2 tons; in 1919, ground limestone was applied at the rate of 1 ton per acre. In the earlier history of the field, hydrated lime had been applied to the whole field in 1898 and in 1905, at the rate of 1 ton per acre each time.

Every plot has received dissolved phosphate which supplied 80 pounds of available phosphoric acid per acre annually. Potash salts were applied to supply 125 pounds of actual potash per acre, but some of the plots received muriate of potash every year, while others received sulfate of potash and magnesia. Three plots received no nitrogenous fertilizer throughout the period, but the rest had applied to them 45 pounds of nitrogen per acre yearly, two receiving nitrate of soda, three sulfate of ammonia, and two dried blood, as the sources of the element.

The distribution of the potash salts and the nitrogenous fertilizers among the plots was as follows:

Plot 1	Nitrate of soda	Muriate of potash
Plot 2	Nitrate of soda	Sulfate of potash and magnesia
Plot 3	Dried blood	Muriate of potash
Plot 4	No nitrogen	Sulfate of potash and magnesia
Plot 5	Sulfate of ammonia	Sulfate of potash and magnesia
Plot 6	Sulfate of ammonia	Muriate of potash
Plot 7	No nitrogen	Muriate of potash
Plot 8	Sulfate of ammonia	Muriate of potash
Plot 9	No nitrogen	Muriate of potash
Plot 10	Dried blood	Sulfate of potash and magnesia

The drains have always discharged most freely in the spring; but have ceased to flow by the time the surface is dry enough to be worked satisfactorily. Seldom has any water run from the tiles during the growing season. Late in the fall, however, there has been some flow shortly before the ground has frozen. The drainage-waters have consequently represented in general the soil conditions after the crops have absorbed all the soluble fertilizers which they required. The few samples secured in the summer season are, however, similar in their relation to their respective plots, to the spring and fall samples.

Most of the data here presented were obtained by Mr. R. W. Ruprecht during the years 1912, 1913 and 1914, in connection with a study of the effects of ammonium sulfate upon the soil. Since then, the writer obtained the summer samples during some abnormally wet seasons, and a few spring samples to check previous observations.

The spring of 1912 followed an unusually cold March and frost was not out of the ground until the last week of that month. In 1913 it was unusually early following a mild winter. The samples obtained in 1914 did not represent the total flow but were secured as a check on the previous seasons. The samples of May 22, 1919, were taken because a fresh application of lime was to be made as soon as the soil could be worked, and these samples would represent the extreme exhaustion of calcium during the period.

The two fall seasons followed somewhat dry summers, although rainfall had been well distributed and crops had not suffered. In 1912, the drains began to discharge after a rainy period of about two weeks, but in 1913 the flow began after an unusually heavy rainfall on the previous day. The three sets of fall samples were each obtained relatively early in the flow from the tiles.

The summer of 1915 was characterized by heavy drenching showers early in July with about six inches of rainfall recorded in six days. The first few days of August were similar. In all probability there was a flow from the drains in July, but other work engrossed our attention. The downpour in August suggested the collection of a summer series of samples, which was made and analyzed. In 1921, moderate rains followed one another closely for a considerable period until at length water appeared at the tile outlets and samples were obtained.

The concentration of salts in the drainage-waters probably varied with the length of time after the flow began from the tile, and the samples may have only approximately represented the composition of the total drainage from a plot. However, it is obviously impracticable to measure and sample accurately by hand, a flow which continues for hours and varies from a mere trickle to a stream as large as the tile will permit.

TABLE 1

Calcium (Ca) in drainage water

DATE		SOIL WITH SODIUM NITRATE	SOIL WITH NO NITROGEN	SOIL WITH AMMONIUM SULFATE	
		Plot 1	Plot 7	Plot 6	Plot 8
		p.p.m.	*p.p.m.*	*p.p.m.*	*p.p.m.*
	Spring				
1912.	April 1	18.0	15.0		31.0
		15.0	11.5		26.5
	April 5	12.0	12.5	27.0	26.5
	April 23	16.5	18.0		33.5
	May 17	18.5	27.0	38.0	42.0
1913.	March 5	24.8	35.2		
	March 9	13.6	28.8	38.9	31.1
	March 14	28.1	28.3	38.1	50.8
	March 21	35.4	42.1	54.5	71.9
	March 28	29.4	41.5	46.7	63.3
	April 5	30.0	46.5	61.4	69.6
	May 29	27.2	42.2	51.6	63.3
1914.	April 9	29.4	41.8	40.8	58.9
	May 6		40.8	49.4	
1919.	May 22	32.8	46.4		66.4
	Fall				
1912.	November 15	27.4	46.3	84.1	81.3
	December 6	32.5	55.0	83.0	68.0
1913.	December 8	28.4	48.0	59.3	69.1
	Summer				
1915.	August 5	36.0	75.6		111.6
1921.	July 21	16.4	27.8		44.2
	Average	24.8	36.5	54.2	

The samples were secured by means of a tin vessel attached to a long wooden handle, by which the vessel could be held under the outlet of the small tile within the well. In the earlier work, the samples were obtained only when the water was running freely from the tile; but later, by producing a sharp edge on the tin and bending it to conform to the curved wall of the well, it was possible to collect the water even when the flow was so scanty that the water ran back on the under side of the tile and spread in a thin film down the wall. The water was transferred from the tin vessel to a glass-stoppered bottle, which had been previously rinsed with some of the sample, and in which the water was kept until analyzed.

Calcium was determined by precipitating it as calcium oxalate, using enough water to yield a satisfactory precipitate on concentrating the solution upon the water-bath. The

earlier determinations were completed by titrating the oxalate with a standard solution of potassium permanganate; but the later results were obtained by igniting the precipitates and weighing the calcium oxide.

Throughout the series, there has persisted the difference in the concentration of calcium in the waters from the three types of fertilizer. The average composition of the different waters shows that the addition of ammonium sulfate to the common mixture of phosphate and potash increased the concentration of calcium 50 per cent, while sodium nitrate decreased it in about the same proportion.

Since there was no way of measuring the amount of drainage-water from each plot, the annual loss of calcium carbonate from the soil cannot be satis-factorily estimated. The concentration of calcium in the waters would undoubtedly have been greater if the application of lime had been made to the whole of each plot instead of to one-half. On the other hand a small part of the calcium must have come from the calcium sulfate which accompanied the phosphate. No other drainage-water analyses that are comparable have come to the writer's attention. MacIntire (7) and Lyon and Bizzell (6) have reported losses of calcium carbonate in lysimeters; but neither nitrate of soda nor sulfate of ammonia were among their fertilizers.

Results with the drainage waters have been corroborated by another distinctly different set of analyses, namely the determination of the residual $CaCO_3$ in the surface soil of each plot. Samples were taken in November, 1920, from the sections that had been most heavily limed. The last application was made in May, 1919, therefore it was about eighteen months afterward when the samples were secured. Since all the lime was applied broadcast to the surface and worked into the soil with a harrow it was considered that borings taken to the depth of six inches would correctly represent the amount of soil that originally contained the $CaCO_3$.

The residual $CaCO_3$ was estimated from the determination of the combined carbon dioxide in the soils, all the analyses of which were performed by Mr. C. P. Jones, who used the method of MacIntire and Willis (8).

It will be noted that the residual $CaCO_3$ in the three soils stands in the reverse order to the calcium in the drainage waters, with the residue in the nitrate soil about twice that in the ammonia soil. It is not considered reliable to estimate the annual losses by calculating the difference between the total $CaCO_3$ applied to the surface and the residue found, because there is no certainty that the supply was not exhausted in the interval between 1913 and 1919, especially on the ammonia plot where crop growth indicated it. The residues found may be those from the last application in 1919. The surface soil might lose $CaCO_3$ faster than would be shown by the drainage-water, because the lower depths would hold some by absorption. This absorption would vary with the fertilizer treatment, for all our work with soil extracts has shown much quicker percolation through the soils from the ammonia plots than through those from the nitrate plots.

At Rothamstead (5) the annual losses of $CaCO_3$ have been computed by comparing the analyses of the soil made forty years apart. In this case the quantity of $CaCO_3$ was so large that there was no question of an exhaustion in the interval and no applications were made during the period. The annual losses were calculated to be 1100 pounds $CaCO_3$ from the ammonia plots and 565 pounds from the nitrate plot.

The marked effect of sulfate of ammonia is due to the hydrolysis of the salt in the soil water, with the formation of H_2SO_4 and NH_4OH. The former will change $CaCO_3$ to $CaSO_4$ while the latter is ultimately nitrified and changes $CaCO_3$ to $Ca(NO_3)_2$.

The lessened amount of calcium in the drainage-water from the nitrate plot may be explained in the following manner. The fertilizers when applied to the soil are in fine, solid particles, fairly well mixed. The soil at the time

TABLE 2

Calcium carbonate in soils, November, 1920

	$CaCO_3$ IN SOIL	$CaCO_3$ PER ACRE SIX INCHES
	p.p.m.	*lbs.*
Plot 1, with $NaNO_3$.............................	1057	1585
Plot 7, with no N................................	789	1183
Plot 8, with $(NH_4)_2SO_4$.......................	518	777

is not very moist and is usually becoming drier as the days pass. The actual moisture with which the fertilizer particles come in contact may not be more than sufficient to form a saturated solution at that point. Further drying of the soil may cause a recrystallization in which will first form crystals of KNO_3 as the least soluble component of the reaction

$$NaNO_3 + KCl \rightleftharpoons KNO_3 + NaCl.$$
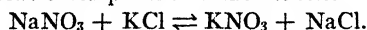
The NaCl will dissolve more quickly and the $CaCO_3$ is less soluble in its presence than with KCl (1). The KNO_3 will be taken up by the growing crop soon after germination is completed, as the salt slowly dissolves.

There is a slight possibility that when NaCl reacts with $CaCO_3$ to form Na_2CO_3 there may be formed a double compound like the mineral gaylussite, which is very insoluble; but little is known about such double carbonates.

SUMMARY

Drainage waters from soils dressed with three typical combinations of chemical fertilizers have been analyzed for calcium at different seasons of the year.

The amount of calcium carbonate removed from the soil where sulfate of ammonia was used was more than twice as large as that where nitrate of soda was the nitrogenous fertilizer.

Nitrate of soda added to an application of dissolved phosphate and muriate of potash protected the calcium carbonate somewhat.

The results with drainage waters were corroborated by the determination of the residual calcium carbonate in the soils of the plots.

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ADSORPTION AND ABSORPTION OF BASES BY SOILS

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The terms adsorption and absorption are used to express the results observed due to contact between the surfaces of different substances or bodies, all of which are endowed with potential energy, either physical or chemical or both, the former being confined to surface area alone while the latter is distributed throughout the entire mass.

Any attractive force due to physical energy alone is a surface area phenomenon and is termed adsorption. Absorption is primarily the result of active chemical forces, but as all substances or bodies are endowed also with physical energy and, as physical forces are exerted at the surfaces of the attracting bodies, the physical phenomenon must precede the chemical and therefore adsorption must take place before absorption. In line of this reasoning absorption may be considered as a physical-chemical phenomenon.

All soils no matter of what origin exhibit to a greater or less degree the phenomena of adsorption and absorption, the substances attracted, of organic or inorganic composition, being derived either directly from the air, the soil atmosphere or from aqueous solutions of substances contained in the soil.

SUBSTANCES IN SOIL WHICH CAUSE ADSORPTION AND ABSORPTION

The existence in the soil of various substances which exhibit the power of attraction and decomposition of certain compounds in solution can be easily demonstrated by the passage of weak solutions of various bases or salts through a given volume of soil. An examination of the extract clearly shows that definite amounts of substances have been removed from the solution used and furthermore the percentage of total abstraction is dependent upon the temperature and concentration of the solutions.

In the treatment of soil with salt solutions it is generally found that double decomposition results to a greater or less degree; the basic ions of the salt solution applied being retained by the soil because of base substitution, while the acid ions, neutralized by the replaced base, are removed by percolation.

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The retention of basic ions illustrates positive absorption, whereas the holding of acid ions, which is possible in some cases, would denote negative absorption.

The soil constituents causing adsorption may be said to include every individual substance of a solid or a partially solid nature contained in the soil, for it has been previously stated that adsorption is a physical phenomenon and is purely related to surfaces alone. The fact that adsorption is wholly concerned with surfaces would be indicative that the degree of adsorption is controlled by the amount of surface area, or in other words, the finer the division of particles concerned the greater the adsorption. From this, one would naturally expect that gelatinous and colloidal substances would be capable of exhibiting a larger degree of adsorption than material in a more coarsely dispersed phase. The question, however, can be raised, in dealing with colloid materials, just where does adsorption end and absorption begin?

Both the degree of adsorption and of chemical reaction are controlled by the fineness of division of the particles concerned. Therefore, it is quite evident that certain observed phenomena may be misinterpreted in terms of adsorption when in reality the effect observed may be due almost entirely to absorption. This is particularly true in those cases in which decomposition takes place, interchange of bases, or when the abstraction of substance is a very appreciable quantity.

It is believed that any substance in the colloid state is as finely divided as it can possibly be and still be almost wholly without the soluble phase. It is also believed that transformation of practically insoluble substances from a dispersoid to the colloid state generally results in a partial solution of the colloid. The fact that a colloid is soluble to a slight degree would favor chemical reactions taking place, the rate and degree of magnitude depending not only upon the solubility product of the colloid in question but also upon the fact of whether or not the product of the reaction is removed from the medium through which the reaction was enabled to take place.

The various soil constituents causing adsorption and absorption are usually termed dispersoids, gels or colloids. It is stated that the weathering of crystallized minerals nearly always yields gels or a mixture of gels (2). Ostwald (1) and many others claim that the products resulting from fermentation and decomposition of organic matter in the soil result in the formation and development of humic compounds which are of a colloidal nature. Therefore there results in the soil the presence of two distinct classes of colloidal substances whose origin and composition is either inorganic or organic. Of the typical inorganic colloids or those gels which occur in the soil three kinds deserve particular mention, namely, silicic acid and the silicates, aluminum hydroxide and its compounds with silicic acid (of which clay is a representative type) and iron hydroxide. The organic colloids, which are of exceedingly great importance are represented largely by that class of substances, rich in carbon and of unknown chemical composition, which are commonly termed humic compounds. To the class of organic colloids. according to Ostwald,

must be added the microörganisms of various kinds—like the soil bacteria—because of the fact of their being microscopical in size, suspensions of them show coagulative phenomena.   To this list must also be added the mucinous substances which are secreted by such soil organisms.

It would not be out of place to include among the living organisms of the soil the various fungi, which are also known to be present, because of their coagulating and adsorptive powers.

SURFACE AREA AND ADSORPTION

That the physical phenomenon, termed adsorption, as exhibited by soils and other material, is most largely controlled by the fineness of division of the particles concerned or by the large surface area resulting from their very small size, is shown by the following tests made with sand and soil under varying conditions.

The sand used was of a pure quartz variety and was previously subjected to a dilute hydrochloric acid digestion, the acid being removed by filtering and washing.   It was then dried at about 80°C., ground and passed through 40-, 60-, 150- and 200-mesh sieves.   Ten-gram portions of sand representing the particles of each size were transferred to small Erlenmeyer flasks and 100-cc. of a series of solutions containing 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 cc. of a standard (saturated) solution of calcium hydrate[2] was added to each flask which was then stoppered and allowed to stand, with shaking for 48 hours.   At the end of this time the solutions were filtered and the free calcium hydroxide was determined by titration of a 50-cc. aliquot with standard hydrochloric acid.

• The soil used is characterized as a silty loam variety and consisted of an air-dried sample taken from the limed end of one of the station plots.   The portion employed consisted of the material which passed through a sieve of 200 meshes to an inch.   Ten-gram portions were taken for the tests which were carried out as with the sand.

The results given in table 1 clearly indicate an increase in the amount of base absorbed with an increase in concentration of calcium hydrate solution used. The reverse is apparent in respect to the percentage of calcium hydrate adsorbed, for the highest percentage adsorption was obtained by the use of the lowest concentration and the lowest with the highest concentration.   It is also noticeable, in the case of the sand, that the larger the surface area the greater the amount of adsorption.   This latter phase is very much more marked in the comparison of results obtained by the use of 40-mesh, 200-mesh, and smaller particles.   With the soil, as with the sand, the amount and percentage of base adsorbed was found to be dependent upon the concentration of the hydrated solution used.

The adsorptive effect as shown by treating previously ignited sand and soil with different amounts of calcium hydrate solution, and the effect produced by evaporating to dryness on the steam bath, both sand and soil, before and after ignition, with different quantities of the solution, is well illustrated in table 2.

[2] One cubic centimeter of the standard (saturated) calcium hydrate solution used was equivalent to 0.00123 gm. calcium oxide.

The results obtained by the use of sand are attributed to a purely physical action, and any observed adsorption may be considered as a rough measurement of the attraćitve force or energy contained in the total surface area represented by the numerous sand particles. The large increase in adsorption as noted by the use of ignited sand is in accord with the above statement, for theoretically at least, with the previous destruction and consequent removal of the thin moisture or water film surrounding each particle of sand grain, contact afterwards with substances in solution should result in an increased extraction and fixation of substances from the solution. This is apparently what has happened in this case for it is inconceivable that any appreciable neutralization of the base occurs as the result of a chemical reaction taking place between the base and a hydrolyzed product of the silica. Any absorption due to chemical reaction must be considered as a negligible quantity.

TABLE 1

Adsorption of CaO from lime-water by sand and soil of different sized particles

LIME WATER IN 100 CC. SOLUTION	CaO ADSORBED FROM 10 GM. SAND OR SOIL									
	Sand between 40- and 60- mesh		Sand between 60- and 80- mesh		Sand between 150- and 200- mesh		Sand finer than 200-mesh		Soil finer than 200-mesh	
cc.	mgm.	per cent	mgm.	per cent	mgm.	per cent	mgm.	per cent	mgm.	per cent
10	0.34	2.80	0.47	3.80	0.98	8.00	2.39	19.40	12.24	99.54
20	0.52	2.10	0.42	1.70	1.08	4.40	3.57	14.50	23.94	97.30
30	0.52	1.40	0.64	1.73	0.44	1.20	3.89	10.53	36.51	98.93
40	0.69	1.40	0.77	1.55	1.30	2.65	4.87	9.90	48.36	98.30
50	0.49	0.80	0.37	0.60	1.06	1.72	4.65	7.56	59.66	97.00
60	0.37	0.50	0.37	0:50	1.38	1.87	4.97	6.73	70.08	94.97
70	0.74	0.85	0.37	0.43	1.72	2.00	5.29	6.14	79.73	92.60
80	0.52	0.53	0.47	0.48	1.87	1.90	5.12	5.20	89.52	90.97
90	0.52	0.47	0.49	0.33	1.70	1.53	5.02	4.53	98.06	88.58
100	0.47	0.38	0.64	0.52	1.99	1.62	5.81	4.72	106.40	86.50

In the case of the soil any plausible interpretation must of necessity be vastly different. The amount of base removed from the solution must be the result of the combination of energy derived from both the physical and chemical properties of the soil grains. Just what proportion may be attributed to each cannot be calculated, for as an increase in the intensity of physical attraction is brought about by a previous dehydration of the soil used, the ignition, although possibly destroying a small portion of the material capable of showing adsorption, is far more destructive to those substances contained in the original soil, which are chemically active toward bases in solution, such as organic and inorganic colloids, various acids and acid salts.

The following reasoning is assumed to explain the much greater basic extraction by the soil compared with that obtained by the sand, and that the greater part of the total base removed from solution is the result of absorption rather than adsorption.

The soil which passed through the 200-mesh sieve must without question represent a larger total surface area than the sand which passed through the same sieve, owing to its silty character. Both increase in surface area and ignition result in an increase in adsorption. It was found that ignition, in case of the sand, increased the adsorption of base approximately six or seven times (table 2, test 3 and 4). If the result obtained with the soil (table 2, test 2) was due to adsorption alone, or even largely to adsorption, then the result obtained with ignited soil (table 2, test 3 and 4) should at least be approximately six or seven times as great as the former. But as this is not the case,

TABLE 2

Comparison of absorption of CaO by fine sand and by soil

TEST NO.	TREATMENT	CaO ABSORBED FROM 10 GM. SAND OR SOIL			
		Sand, 200-mesh		Soil, 200-mesh	
		gm.	*per cent*	*gm.*	*per cent*
1	50 cc. H_2O + 50 cc. $Ca(OH)_2$.........	0.00494	8.04	0.05966	97.00
2	100 cc. $Ca(OH)_2$.....................	0.00777	6.32	0.10640	86.50
3	Material previously ignited 50 cc. H_2O + 50 cc. $Ca(OH)_2$.................	0.02641	42.94	0.04854	78.92
4	Material previously ignited 100 cc. $Ca(OH)_2$..........................	0.04809	39.10	0.10573	85.96
5	50 cc. $Ca(OH)_2$ added, evaporated to dryness, made up to 100 cc. with H_2O.	0.04873	79.24	0.06118	99.48
6	100 cc. $Ca(OH)_2$ added, evaporated to dryness, made up to 100 cc. with H_2O.	0.10652	86.60	0.12152	98.80
7	50 cc. $Ca(OH)_2$ added to ignited material, evaporated to dryness, made up to 100 cc. with H_2O.............	0.06128	99.64	0.05786	94.01
8	100 cc. $Ca(OH)_2$ added to ignited material, evaporated to dryness, made up to 100 cc. with H_2O.............	0.11476	93.30	0.11493	93.44

and as the results are quite similar in both instances, it is evident that absorption played a greater part than adsorption in the soil.

The results derived by evaporating the mixtures of sand or soil with calcium hydrate solution to dryness upon the steam bath are considerably higher than the results obtained in the other treatments, especially in reference to sand. These results may be looked upon as not comparable to those obtained without the aid of evaporation for the following clearly apparent reasons:

1. The influence of heat during the evaporation facilitates an increase in any chemical reaction.

2. Differences in the length of time the mixture of sand or soil and calcium hydroxide is allowed to remain on the steam bath after dehydration has been accomplished would mean variations in the amount of free base found as afterwards determined in the solution.

3. The longer the time for the evaporation and total exposure of the calcium hydroxide to the atmosphere the greater the amount of carbonation of base.

4. Another source of error is due to the fact that carbonation of the calcium hydrate takes place during the process of filtration and to some extent during the time consumed in titrating. The rate of change of hydrate to carbonate depends upon the amount of carbon dioxide in the atmosphere during the process of manipulation, and also, is proportional to the concentration of the solution. Therefore in the employment of calcium hydrate solutions of increasing strengths there would naturally result corresponding increases in carbonate formed, which expressed in terms of the experiment would show progressive increases in basic adsorption.

ABSORPTION EXPERIMENTS

Differentiation between the amount of base adsorbed and absorbed is clearly impossible by the use of lime-water or any other solution of pure base, for the amount of free base left in solution, unacted upon, is the difference between the total amount of base contained in the solution added to the soil, and the amount withdrawn from solution or neutralized, under ordinary conditions, by the combined effects of surface area energy and molecular or ionic energy. If adsorption is a purely physical action and absorption the results of chemical attractions, then there should exist some means of estimating, to some extent at least, the amount of base absorbed by any given soil. By the employment of certain salt solutions and through mass action, it is believed that basic absorption may be estimated with fair accuracy. This belief is based on the fact that accompanying base absorption there results a corresponding degree of salt decomposition, and therefore a measurement of the liberated acid ions in solution will be indicative of the amount of base any given weight of soil will bc capable of extracting from solution.

The amount of base that a soil will actually absorb is dependent upon the character and composition of the salt used, for hydrolysis, and the factors influencing the hydrolysis of a salt in aqueous solution, are of primary importance in the calculation of the basic absorptive capacity of any given soil.

Calcium carbonate in the precipitated form was selected as the salt for the following reasons:

1. Carbon dioxide resulting from the decomposition of the carbonate is indicative of chemical reactions or absorption, and is readily measured.

2. This easily decomposable, weakly basic salt is the soil corrective most generally used.

3. Precipitated calcium carbonate is susceptible to the action of very slight concentrations of hydrogen-ions.

4. Carbonate of lime has a low solubility product and the degree of hydrolysis is affected only to a very slight degree by changes in room temperature.

The principle involved in the following method is based on a modified Tacke method which consists in the addition of CO_2-free distilled water to a given weight of a soil or other material and precipitated chalk or other carbonates. Any carbon dioxide resulting from the reaction is removed by the passage of carbon dioxide free air through the solution. The amount of liberated carbon dioxide determined constitutes the measurement of basic absorption.

DESCRIPTION OF METHOD

The apparatus employed is original and so designed as to enable the operator to make four distinct tests at the same time and also facilitates the use of solutions of carbonates (molar) as well as carbonates in the solid state. When the latter are used the carbonate is added to the soil or other material contained in small Erlenmeyer flasks which are then connected to the apparatus. Before adding the water, which furnishes the only medium through which a reaction between the reactive substances and the hydrolyzed products of the carbonate can take place, any free carbon dioxide is removed from the flasks and apparatus by drawing CO_2-free air (by suction) through the apparatus. In the experiments in which solutions of carbonates are employed, the preparation for the tests is somewhat modified. As four separate tests are carried out simultaneously and each equal weight of soil is treated with an equal volume of solution but of different concentrations, it is necessary to supply individual openings to each flask for the admittance of the solutions used. This is accomplished by inserting pieces of glass tubing, provided with short pieces of rubber tubing at the ends, through the rubber corks of the Erlenmeyer flasks containing the material to be tested. These individual openings, and the employment of attached rubber tubing, allow for the addition of the carbonate solutions to the material without change in concentration and moreover without admitting atmospheric carbon dioxide to the flasks. After the addition of the solution to the flask the aperture is made air-tight by plugging with a piece of solid glass tubing or by the use of a pinchcock.

PROCEDURE

Fifty grams of air-dried soil or other material (the weight taken depending upon the bulk) are transferred to small Erlenmeyer flasks. Definite weights of carbonates (alkali or alkaline earth) are added to the material in the flasks, which are then connected to the apparatus. If solutions of carbonates are used the material whose basic absorptive power is to be obtained is transferred to the flasks and attached to the apparatus. Carbon-dioxide-free air is then drawn through for five minutes to replace the air in the flasks and apparatus. Known volumes of standard $Ba(OH)_2$ solution (approximately 0.05 N standardized against 0.1 N HCl) which has been protected from atmospheric carbon dioxide, are measured from a burette into a series of four small Erlenmeyer flasks which constitutes the train carrying the absorption solution for each separate test. The four series of absorption flasks are connected to the apparatus.

When using solid carbonates, 50 cc. of distilled water are added to each flask by means of the separatory funnel.

When using carbonate solutions, 50 cc. volumes of carbonate solutions, containing definite weights of dissolved carbonates as described above, are added.

After the addition of the water or the carbonate solutions the flasks are shaken as a unit for a period of thirty minutes, during which time air is being constantly drawn through the mixture. The passage of air is continued, with shaking of flasks every now and then, for four hours. The evolved carbon dioxide is swept out of the reaction flasks into the absorption flasks where it is retained as barium carbonate. The excess of standard $Ba(OH)_2$ solution is then determined by titrating with 0.1 N HCl, using phenolphthalein, or better, thymolphthalein[3] as indicator.

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[3] Thymolphthalein is preferred as an indicator in this case because its use makes possible a more definite end-point. Its superiority is especially noticeable in the presence of considerable amounts of $BaCO_3$. The value of this indicator is due to its slightly higher pH value which consequently decreases the sensitiveness to a slight degree toward the hydroxyl-ions resulting from the hydrolysis of the $BaCO_3$ precipitate.

Blank tests are made by using same volume of water and same weight of carbonate. The amount of carbon dioxide, resulting from the absorptive decomposition of the carbonate used, minus the carbon dioxide obtained in the blank tests, in terms of the base of the carbonate used represents the basic absorption of the material tested. ·

It is plainly evident upon consulting table 3 that absorption is directly based upon the hydrolysis of the salt used. The salts composed of the weaker bases

TABLE 3

Absorption by an unlimed soil of the bases from different carbonates expressed in terms of evolved CO_2

SOLUTION USED		CO_2 FROM 10 GM. SOIL	SOLUTION USED		CO_2 from 10 GM. SOIL
		mgm.			*mgm.*
0.001 M		0.4	0.015 M		6.3
0.01 M		3.9	0.03 M		7.9
0.02 M		5.3*	0.046 M		6.3
0.03 M		5.7*	0.06 M	K_2CO_3	3.8
0.04 M		4.8*	0.12 M		1.2*
0.05 M	Li_2CO_3	3.2	Saturated solution		0.2*
0.10 M		1.6	0.06 M	$NaHCO_3$	15.3
0.20 M		1.2	0.12 M		19.7
0.01 M		3.7	0.06 M	$KHCO_3$	22.4
0.02 M		4.6	0.12 M		18.0
0.03 M		4.4	0.06 M	$MgCO_3$†	5.7
0.04 M		4.4*	0.12 M		5.2
0.05 M	Na_2CO_3	4.3	0.06 M	$CaCO_3$†	6.0
0.06 M		2.4*	0.12 M		6.7
.. 0.10 M		1.1	0.06 M	$SrCO_3$†	3.1
0.20 M		1.0	0.12 M		5.1
0.50 M		0.7	0.06 M	$BaCO_3$†	7.5
Saturated solution		0.3*	0.12 M		6.6

* Average of two determinations.

† Very slightly soluble in water but expressed in molar terms for comparison.

(alkaline earth bases) are absorbed to a greater degree than are the salts composed of the stronger alkali bases (lithium, sodium, and potassium). This holds only in the comparison of the neutral salts for it is seen that the base of the acid salts (bicarbonate) of sodium and potassium are absorbed to a greater extent than the bases of the neutral salts. From the standpoint of hydrolytic dissociation the acid salts are hydrolized to a greater degree than neutral salts. It is believed that the bicarbonate of the alkaline earth metals,

such as barium and calcium would show a larger basic absorption than the bicarbonates of the alkali metals. The concentration of the more soluble carbonates influences to a larger degree the base absorption as shown in table 3. The percentage of base absorbed decreases with the concentration of solution, being highest in the case of the weakest concentration and lowest in that of the greatest concentration, or the saturated solution. The amount of base

TABLE 4

Effect of temperature upon absorption

Ice Water vs. Room Temperature

NO.	SALT	CONCENTRATION OF SOLUTION USED (50 CC.)	CO₂ OBTAINED		BASE EQUIVALENT (ABSORBED)	
			At ice water temperature	At room temperature	At ice water temperature	At room temperature
			gm.	gm.	gm.	gm.
1	Na_2CO_3	0.04 M	0.00834	0.02252 (av. of 3)	0.01177	0.02973
2	Li_2CO_3	0.04 M	0.00884	0.02405 (av. of 2)	0.00602	0.01640

Hot Water Bath vs. Room Temperature

NO.	SALT	CONCENTRATION OF SOLUTION USED (50 CC.)	CO₂ OBTAINED		BASE EQUIVALENT (ABSORBED)	
			At water bath temperature	At room temperature	At water bath temperature	At room temperature
			gm.	gm.	gm.	gm.
1	Na_2CO_3	0.01 M	0.04240	0.01863	0.05975	0.02625
2		0.02 M	0.05368	0.02288	0.07564	0.03224
3		0.03 M	0.04078	0 02218	0.05746	0.03125
4		0.04 M	0.04150	0.02252	0.05848	0.02973
5		0.05 M	0.02376	0.02138	0.03348	0.03012
6		0.06 M	0.02526	0.01267	0.03559	0.01785
7	Li_2CO_3	0.04 M	0.05896	0.02405	0.04020	0.01640
8	$CaCO_3$	2.0 gm.	0.06378	0.03020	0.08131	0.03850

absorbed is variable, increasing from the weakest concentration until a certain definite concentration is reached which represents the maximum absorption. Beyond this point, which is probably different with different salt solutions, an increase in concentration results in a decrease in absorption. Saturated solutions show practically no absorption of base.

The effect of temperature upon absorption was obtained by placing the flasks containing 50 gms. of an unlimed soil and 50 cc. of carbonate solutions for 2 times into a mixture of snow and water and in water which had been heated to the temperature of the steam bath. The results are given in table 4.

The results given in table 4 substantiate more fully the statement made above, that the amount of absorption depends upon the degree of hydrolysis of the salt used, for hydrolytic action is increased with increase in temperature.

This difference in the hydrolysis of salts and the factors governing hydrolysis is thought to explain, largely, the different results obtained by the use of the various soil acidity methods.

EVIDENCES THAT THE DECOMPOSITION OF CARBONATE OF LIME BY SOILS IS DUE TO THE PRESENCE OF REACTIVE CHEMICAL CONSTITUENTS AND NOT TO SURFACE AREA

The following tests are offered as evidence that, in the absence of reactive chemical substances, surface area takes no part in the decomposition of calcium carbonate by soils. The method employed in making these tests as well as all following tests in which carbonates are used has been previously described.

Sand

The sand used in this instance was a representative sample of a large mass of sand which had been deposited upon the shore of the Connecticut River by current and wind action. It was selected as representative of the more resistant mineral constituents of the soils of the valley drained by the Connecticut River. After pulverization in a procelain mortar this soil had, with one exception, the physical appearance of the soils of the station plots. It was a little less highly colored. Upon shaking this finely powdered sand with water a turbidity resulted which was greater in comparison than the turbidity produced with the soils from the different plots; filtration was found to be more difficult, and the filtrate more cloudy. This sand showed a basic absorption which was equivalent to 0.00007 gm. $CaCO_3$ (1 gm. sand). Two million pounds of this finely pulverized sand would show a basic absorption equivalent to 140 lbs. $CaCO_3$.

Clay

Clay is usually mentioned as one of the best means of illustrating surface adsorption. There can be no question as to the fine state of division of the clay particles and the enormous surface area. The sample of clay used was of an exceptionally pure variety obtained on the shore of the Connecticut River from the bed of a brook. The water running over the surface of this clay was very clear and pure. The amount of carbon dioxide obtained, by several treatments of 50 gm. of clay and 1 gm. of precipitated chalk according to the method previously described, was so small that it may be considered negligible. The quantity expressed in terms of carbonate decomposed, however, was equivalent to 0.00002 gm. $CaCO_3$. Two million pounds of this clay would absorb an amount of base equivalent to approximately 40 pounds of $CaCO_3$.

A qualitative test made upon a sample of this clay showed, as expected, an abundance of iron and aluminum but no calcium. The iron and aluminum were present as complex silicates.

It is plainly evident from the results of this experiment that the enormous surface area of this clay had no adsorption influence upon the base of the carbonate.

As a further test for surface adsorption, pumice was tried. Pumice is a peculiar vasicular variety of feldspathic lava. It was ground very finely in a mortar and the basic adsorption as shown by test was very small. The amount of carbon dioxide obtained was 0.0000028 gm. for 1 gm. of pumice. This is equivalent to 0.000006+ gm. of $CaCO_3$. Two million pounds of this pulverized pumice, representing a very large surface area, would be capable of adsorbing an equivalent to only 12 pounds $CaCO_3$.

In consideration of all the above tests there seems to be some evidence indicating that surface area alone plays practically no part in the decomposition of calcium carbonate and on the other hand any observed decomposition of carbonate is the result of chemical action, brought about by the presence of weak acids or by other reactive chemical substances.

HYDRATED SILICA AND ALUMINA

It is believed that the rate and intensity of any possible reaction between the above colloidal substances and limestone must be extremely slight because of the chemical nature of the substances involved. Any slight reaction with lime is thought to be due to the formation of weak acids brought about by the very slight hydrolytic dissociation of the hydrated substances. The faintly acid character of the colloidal solutions of hydrated alumina and silica was shown by the appearance of a slight pink coloration upon application of methyl red as indicator in the hyrogen-ion concentration test.

It is plainly evident that the result of such a determination is entirely dependent upon the purity of the substances which are brought into contact with the limestone. With the above fact in mind great care was exercised in the preparation of the colloidal solutions. The hydrated alumina and silica were first precipitated from solution, transferred to Büchner funnels and well washed with distilled water. The gelatinous masses were then transferred to specially constructed dializers and the process of purification was continued for many months, after which the hydrated products were washed into large Erlenmeyer flasks. Washing by decantation was then resorted to and this operation was repeated until the colloid preparations showed by indicator tests no change in the slight hydrogen-ion concentration.

Approximately 20- and 30-cc. portions of the well-shaken gelatinous mixtures were taken for experimentation. One-half gram of precipitated chalk and a small amount of water were added to each flask and CO_2-free air was drawn through each flask for four hours.

It was found that 0.0025 gm. CO_2 in one case and 0.0014 gm. in the other resulted from the action of precipitated chalk upon hydrated alumina in the presence of water. With hydrated silica 0.0036 gm. CO_2 was obtained in each case. The experiment was continued the next day, without disconnecting the

flasks containing the hydrated products, and after running another four hours 0.0013 and 0.0012 gm. CO_2 was obtained with aluminum hydrate and 0.0014 and 0.0009 gm. CO_2 with the hydrated silica.

In view of the fact that the indicator test showed a slight acidity it is believed that the decomposition of the small amount of $CaCO_3$ was due to absorption of the base and not to adsorption.
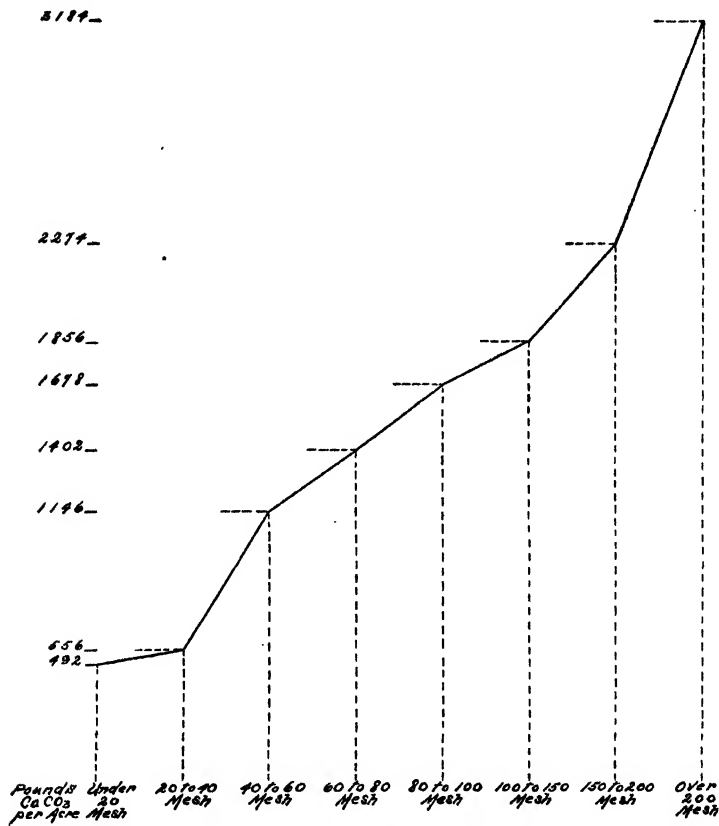
FIG. 1. GRAPH SHOWING THE DEGREE OR VELOCITY OF THE REACTION BETWEEN A SOIL AND CARBONATE OF LIME AS INFLUENCED BY THE FINENESS OF THE CARBONATE

RATE OF DECOMPOSITION OF $CaCO_3$, OR THE RATE OF ABSORPTION OF THE BASE, CaO

The rate of absorption of CaO is dependent upon the size of the $CaCO_3$ particles which are brought into contact with the moist soil and furthermore, which is self-evident, the rate is also dependent upon the mass of $CaCO_3$ up to a certain point.

The results in table 5 were obtained by the treatment of 50 gm. of an unlimed soil with 1 gm. of $CaCO_3$ of different sized particles[4] using the same general method.

The results obtained are in agreement with the old experiments of G. Stas, cited by Ostwald (1, p. 72) who found the solubility of silver chloride in the precipitated form (in other words, as particles of approximately colloid size) to be a hundred times greater than the solubility of this same substance when granular or coarsely dispersed. This behavior is not peculiar to silver chloride, but holds for all solid substances. It is also plainly evident that the velocity of the reaction between the soil and carbonate, measured in terms of carbon dioxide is in accord with Wenzel's law, which reads: "the reactive velocity of solids with liquids is proportional to the area of contact."

The data in table 5 with representative graph, figure 1, are of value for illustrating the availability of limestone of different degrees of fineness when applied to the soil. The fact that the rate of absorption is controlled largely

TABLE 5

Effect of fineness of $CaCO_3$ on the absorption of base

NO.	DEGREE OF FINENESS OF $CaCO_3$	CO_2 PER GRAM OF SOIL	$CaCO_3$ EQUIVALENT	REACTING $CaCO_3$ PER ACRE OF SOIL (2,000,000 LBS.)
		gm.	*gm.*	*lbs.*
1	Less than 20-mesh.............	0.000108	0.000246	492
2	Through 20-mesh..............	0.000122	0.000278	556
3	Through 40-mesh..............	0.000252	0.000573	1146
4	Through 60-mesh..............	0.000308	0.000701	1402
5	Through 80-mesh..............	0.000369	0.000839	1678
6	Through 100-mesh.............	0.000408	0.000928	1856
7	Through 150-mesh.............	0.000500	0 001137	2274
8	Through 200-mesh.............	0.000700	0.001592	3184

by the surface area of carbonate particles denotes that any appreciable decrease in the amount of carbonate used in the above tests would result in greater comparative differences. It is evident that a certain definite total surface area of particles is necessary to obtain a maximum absorption within a given time. Any increase in surface area beyond that required for maximum absorption will produce no acceleration in the rate of absorption, (table 6), but a decrease in the total surface area below the amount required to attain the maximum amount will result in a corresponding decrease in rate of reaction. The deduction is plain that if 0.5 or 0.25 gm. of $CaCO_3$ were used in place of the 1 gm. greater comparative differences in the rate of absorption would have been obtained.

The results in table 5 indicate the advisability of applying the finer grades of carbonate of lime to the soil whenever a quick response, in terms of a reduc-

[4] Different sized particles of $CaCO_3$ were obtained by grinding marble in a mortar and using sieves of different meshes.

tion of the hydrogen-ion concentration is desired or whenever a deleterious soil environment, due to the presence of excessive amounts of certain toxic salts, is to be remedied.   With an increase in fineness of particles there results an increase in the degree of basic activity of the limestone, as measured in terms of velocity reaction.   The rate of absorption of CaO would progressively increase until the carbonate was obtained in the finest condition possible, amorphous, approaching the colloid state.

It has been proved that different amounts of soluble carbonates greatly influenced the degree of absorption (table 3).   It has also been proved that the rate of absorption is dependent upon the frequency of contact between soil and carbonate particles in a water medium (table 5).   With these facts in mind an experiment was undertaken for the purpose of showing that varying amounts of $CaCO_3$, in a very fine state of division, produce no changes in the rate of absorption, provided the carbonate is present in excess of the amount actually required to complete the reaction.   Fifty grams of an unlimed soil was treated in the usual way with 0.25, 0.50 and 1.00 gm. of precipitated chalk.   The

TABLE 6

Relation of different amounts of precipitated $CaCO_3$ to absorption

$CaCO_3$	CO_2 1 GM. SOIL	$CaCO_3$ EQUIVALENT 1 GM. SOIL	REACTING $CaCO_4$ PER ACRE (2,000,000 LB. SOIL)	$CaCO_3$ EQUIVALENT PER ACRE APPLIED (2,000,000 LB. SOIL)
gm.	*gm.*	*gm.*	*lbs.*	*tons*
0.25	0.000633	0.00144	2880	5
0.50	0.000619	0.00141	2820	10
1.00	0.000623	0.00142	2840	20

quantities of $CaCO_3$ used are equivalent to the application of 5, 10 and 20 tons of limestone per acre basis (2,000,000 pounds of soil).

The results given in table 6 plainly show that the different amounts of $CaCO_3$ used had no effect upon the degree of base absorption.   This is because the solubility of calcium carbonate is very small and the maximum solubility is easily reached by a small amount of calcium carbonate.   It must be borne in mind, however, that 100 per cent base absorption is very likely an impossibility and therefore the amount of base present must be many times greater than the amount of base that is capable of being absorbed.   In case of substances which have a low solubility product consideration must be taken of the fact that the rate of action is to a large extent dependent upon the surface area and the number of particles which come into contact with the absorbing material.

OTHER ABSORPTION EXPERIMENTS

Experiments were carried out for the purpose of ascertaining whether or not a soil, after having absorbed a quantity of base which was considered a maximum amount, was capable of showing further basic absorption.

The absorption of base was obtained in the usual manner. The soil to which water and calcium carbonate had been added was transferred to a Hirsch funnel and filtered and washed with distilled water. After a long and thorough washing the soil was removed from the filter and dried at room temperature. After it was well dried a second absorption test was made in the same way after the addition of more precipitated chalk. The amount of carbon dioxide obtained was very slight, indicating that the soil had previously absorbed a maximum amount or very nearly this quantity of base. The small amount of carbon dioxide obtained in this second instance might be laid to some cause other than a reaction between soil and carbonate, as absorption of carbon dioxide from the atmosphere and carbon dioxide from bacteria activity. This laboratory experiment agrees with the result obtained in case of soil 5, table 7.

Other experiments were made to determine the base absorbing power of soils which had previously been treated or digested with hydrochloric acid. It was found that after removing all lime from the soil, the basic absorption was increased, the increase depending upon the amount of lime which had been added to the soil in the field.

Fifty grams of 100-mesh soil, taken from fertilizer experiment plots, were treated with 0.5 gm. of precipitated $CaCO_3$ and the absorption values were obtained in the usual way (results given in table 7). After completing this test the soil was filtered through a Hirsch funnel and thoroughly washed. This filtrate was saved. The soil was then transferred to an Erlenmeyer flask and an excess of dilute hydrochloric acid was added. The digestion was either hot or cold. After several hours digestion the soil was again transferred to a Hirsch funnel and filtered and washed until there resulted a constant hydrogen-ion concentration, as shown by use of indicator. (It was found that a soil exhibited two phases of acidity, which might be termed active and potential acidity.) The soil was then dried at room temperature and afterwards the absorption test was again made. Results are given in table 7. The soil was again filtered and this filtrate was added to the first.

The filtrate from each absorption test was evaporated to dryness. The resulting residue was of appreciable quantity, light colored and of low specific gravity. This residue upon analysis was found to contain K_2O and P_2O_5. This test seems to indicate that lime has a replacement power and that K_2O and P_2O_5 are made available.

The results given in table 7 clearly prove that a soil after acid treatment and after all traces of the acid have been removed, is capable of greater basic absorption. This absorption was increased three to four times in all cases but one. The exception was soil 5, taken from a lime plot, and the absorption in this case amounted to an increase of about twenty-five times.

The effect of continuing the acid-followed-by-lime treatment upon the absorbing material contained in the soil was determined by subjecting a number of the same samples of soils used, 1, 2, 3, 4, to a second acid treatment and the amount of base absorbed again determined. The difference in absorption of CaO, per gram of soil, amounted to 0.00037, 0.00045, 0.00045 and 0.00048 gm. respectively. It is seen from these results that a continuation of such a treatment decreases the absorbing power of a soil but slightly. Large amounts of both iron and aluminum were removed from the soil by acid digestion and

yet the absorption of CaO still persisted. The slight decrease in the degree of base absorption may be accounted for in either of two ways. First, each digestion of soil with acid may be destructive to a slight degree to the absorbing material, and second, the absorbing material reacting with lime may be rendered slightly soluble and so is thus removed, in small quantities, from the soil.

It was further noted that the total basic absorption (after acid treatment) in terms of calcium oxide was approximately equal to the initial absorption (made on the original soil) plus the CaO (in the original soil). This would indicate that the CaO absorption is dependent upon the amount of calcium already in combination in the soil. The result obtained in case of soil 5 (lime plot) substantiates this statement.

TABLE 7

Absorption of CaO by soil before and after treatment with HCl

SOIL	CO_2 BASIS		$CaCO_3$ BASIS		REACTING $CaCO_3$ ACRE BASIS 2,000,000 LB. SOIL	
	Before	After	Before	After	Before	After
	gm.	gm.	gm.	gm.	lbs.	lbs.
1	0.0003230	0.0014545	0.0007344	0.0033070	1469	6614
2	0.0003289	0.0015016	0.0007479	0.0034141	1496	6828
3	0.0003098	0.0014917	0.0007044	0.0033917	1409	6783
4	0.0004103	0.0017893	0.0009331	0.0040683	1866	8137
5	0.0000618	0.0015840	0.0001406	0.0036016	281	7203
6	0.0002334	0.0012899	0.0005308	0.0029342	1062	5868
7	0.0004488	0.0019338	0.0010206	0.0043968	2041	8794
10	0.0004941	0.0019409	0.0011237	0.0044130	2247	8826
11	0.0005144	0.0023028	0.0011697	0.0052360	2339	10472
12	0.0004752	0.0019965	0.0010807	0.0045395	2161	9079
13	0.0003980	0.0017575	0.0009050	0.0039961	1810	7992
14	0.0004156	0.0018788	0.0009451	0.0042720	1890	8544

INFLUENCE OF SOLUBLE SALTS UPON THE ABSORPTION OF BASE

That the presence of soluble salts in the soil influences lime absorption can be easily demonstrated by laboratory experiments carried out in the same manner as the preceding absorption tests. To 50 gm. of two unlimed soils was added 1 gm. of C.P. salts in one case and 1 to 2 gm. of commercial salts in the other. All tests were carried out for a period of three hours with results shown in table 8.

The results given in table 8 clearly indicate that the degree of absorption as exerted by the presence of other salts depends largely upon their chemical nature, and the subsequent decomposition of $CaCO_3$, may range from a very small to a large amount. The differences in absorption are very striking in those cases in which $(NH_4)_2 SO_4$, $FeSO_4$, and calcium cyanamide are used. It is very clear that a reaction took place between the $(NH_4)_2 SO_4$ and $CaCO_3$,

and $FeSO_4$ and $CaCO_3$. It is also evident upon consulting numbers 4, 7, and 12 that the soil was a factor in increasing the rate of decomposition of carbonate. The low absorption obtained when calcium cyanamide was used is thought to be due to the greater degree of hydrolysis of calcium cyanamide rather than the carbonate. The fact that the cyanamide and carbonate both contain like ions (Ca) might be given as a cause for the low absorption, but preference is given to the former theory.

The action of calcium carbonate upon soluble salts of aluminum and manganese was also illustrated. To a solution of the sulfates of aluminum and manganese, calcium carbonate was added. The mixtures were shaken and allowed to stand for some time. The results obtained clearly showed that

TABLE 8

Absorption of CaO in the Presence of other salts

NO.	PRECIPITATED CHALK	SALT USED	CO_2 OBTAINED
	$gm.$		$gm.$
Soil A			
1	1	$CaSO_4$	0.01467
2	1	$MgSO_4$	0.02141
3	1	Na_2SO_4	0.01483
4	1	$(NH_4)_2 SO_4$	0.02937
5	1	$FeSO_4$	0.06805
6	1		0.01324
Soil B			
7	0.5	1 gm. $(NH_4)_2 SO_4$	0.03012
8	0.5	2 gm. acid phosphate	0.01481 *
9	0.5	2 gm. acid phosphate and 2 gm. calcium cyanamide	0.00024
10	0.5	2 gm. calcium cyanamide	0.00021
11	0.5		0.01559†
No soil			
12	0.5	1 gm. $(NH_4)_2 SO_4$	0.00722

* Average of two.

† Average of three.

aluminum was precipitated as $Al(OH)_3$ and the manganese as a brown oxide, probably as Mn_3O_4, or a basic oxide. The aluminum was precipitated quite readily whereas a much longer time was required to remove the manganese from solution, as oxygen is necessary to bring about the latter reaction. The experimental evidences obtained by the above tests are of help in explaining the reason why absorption tests in general are unreliable in the sense of expressing the lime requirement of a soil.

DISCUSSION OF RESULTS

It is not assumed that the amount of calcium absorbed, as shown by this method, expresses numerically the number of pounds of calcium carbonate that

should be applied per acre of soil and consequently construed as an exact
lime requirement method. In general, however, a large absorption indicates
that the soil so tested is deficient in lime for the normal and optimum growth of
crops which are dependent upon this basic element either as a direct plant food
or to give the proper reaction for plant development. A soil that has received
a dressing of lime may show by the absorption test that it is capable of absorb-
ing still more lime, and yet there may be present a sufficient amount of lime to
satisfy the physiological needs of the plant, and also to act as a soil corrective.

The absorptive capacity of a soil for lime is influenced by previous lime and
fertilizer treatment and consequently is less than the total basic absorptive
power of the soil. This point is well illustrated in case of soil 5 which during
the years 1899 to 1919 had received nothing but a yearly application of lime
together with additional amounts upon the several occasions when the whole
field was limed. Manure and a commercial fertilizer consisting of a mixture
of barium sulfide and apatite were added in 1919, and in 1921 manure alone
was added. The absorption test made upon a sample of this soil, collected in
1921, showed so slight a basic absorption that it was a question of whether or
not the results obtained were due to basic absorption or to occluded carbon
dioxide in the soil, the source of the latter probably being bacterial. (See
table 7.) The results obtained would indicate that this soil had very little
lime-absorbing power, but the reason for the very small degree of absorption
noted is plainly apparent upon consideration of the total amount of lime
which has been added to the soil of this plot.

The amount of residual $CaCO_3$ determined in this soil approximated 3000
pound per acre (method of Assoc Off. Agr. Chem.). The results of both
tests clearly prove that this soil had absorbed lime to its utmost capacity.

The causes of a high lime absorption shown by some soils are:

1. The presence of a large amount of humic substances in the soil (humic compounds
and acids) which are very reactive with lime.

2. A high hydrogen-ion concentration resulting from the presence of acids, principally
organic and carbonic, and acid salts, such as sulfates of the weakly basic elements, ferrous,
ferric, and aluminum sulfates.

whereas a low lime absorption denotes the following:

1. A very poor and unproductive soil deficient in humus, like sand and clay.

2. A soil containing a sufficiency or superabundance of lime (as calcium humates and
carbonates).

SUMMARY

The colloids present in soils may be conveniently divided into two classes,
inorganic and organic. The forms commonly comprising the class of inorganic
colloids are silicic acid and the silicates, aluminum hydroxide and its compounds
with silicic acid and iron hydroxide. The different kinds included in the
organic class of colloids are the humic compounds and the various kinds of

microörganisms, like the soil bacteria and fungi and the mucinous substances which are secreted by such organisms.

Colloids are capable of showing adsorption and absorption. Adsorption, which is a surface area phenomenon, is believed to be very small, whereas absorption, which might be termed adsorption-decomposition, or in plain terms, a physico-chemical reaction, is quite large, depending upon the chemical nature of the reactive colloids.

The absorption of bases by soils is directly dependent upon the degree of hydrolysis of the salt in solution. The laws governing hydrolysis therefore would apply to absorption, namely: chemical constitution of the salt, concentration and temperature.

The absorption of bases of compounds containing a highly ionized base and acid is small. A decrease in the ionization of both base and acid results in an increase in the degree of hydrolysis and consequently an increase in base absorption.

The absorption of the base of substances which have a small solubility product is in accordance with Wenzel's law: the reactive velocity of solids with liquids is proportional to the area of contact.

CONCLUSIONS

The absorption of bases by a soil is due to chemical reactions between soil constituents and the dissolved salt. Adsorption or surface attraction of colloids is only an accessory. These facts have been shown by the measurement of the CO_2 released by the reactions.

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MICROBIOLOGICAL ANALYSIS OF SOIL AS AN INDEX OF SOIL FERTILITY: VIII. DECOMPOSITION OF CELLULOSE[1]

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Among the constituents of plant residues, green manures and stable manure added to the soil, cellulose occupies an important place. A study of the organisms concerned in the decomposition of cellulose, including bacteria, fungi and actinomycetes, has occupied the attention of many investigators and any new contribution to this subject has always aroused great interest. As a matter of fact it has not been definitely established as yet just how far celluloses are broken down by microörganisms, the chemistry of the process being in most cases, still an open question. Until the development of Charpentier's (3) method, there was no adequate method for the quantitative determination of cellulose in the soil. Most of the studies on cellulose decomposition in the soil by microörganisms have been limited to qualitative results, such as the mechanical disintegration of filter paper, formation of pigments and growth of organisms on the paper, formation of clear zones around the colonies on cellulose agar, gas formation, etc.

By means of an accurate quantitative method it is possible to study the rapidity of cellulose decomposition in different soils, as influenced by soil type, physical and chemical condition, micro-flora, etc.

Christensen (4) was the first to suggest that the power of a soil to decompose cellulose may serve as an index of soil fertility. A definite amount of the soil to be investigated was placed in Erlenmeyer flasks so as to cover four-fifths of the bottom of the flasks. The water was added from a pipette to the uncovered part of the bottom of the flask. A few strips of filter paper were then pressed upon the soil, which was kept moist all the time. From nine to ninety-three days were required for the complete decomposition of the paper, depending upon the soil. Christensen (5) has further shown that the physical condition of the soil as well as its reaction do not influence greatly its cellulose-decomposing capacity. The presence of available minerals, primarily phosphates, as well as available nitrogen, are of first importance, and, in some cases, also the microbial flora; in other words the phenomenon of cellulose decomposition is influenced by the chemical and microbiological soil conditions. The amount of cellulose decomposed is governed by the available nitrogen and phosphates in the soil. In general, the chemical composition of the soil was found to be of much greater importance to the cellulose decomposition than the microbial flora. Only in the case of certain peat soils, did the inoculation with cellulose-decomposing bacteria have any effect. By the use of Christensen's method, Arnd (1) found that fertilized, limed and cultivated peat soils possessed a

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greater cellulose-decomposing power than untreated peat soil; the soil treated with stable manure was most active.

Mütterlein (7) criticised Christensen's method as allowing the development of only aerobic organisms and not allowing for the influence of moisture, and other soil conditions. He suggested the placing of one or two pieces of filter paper of a uniform weight, 10–20 gm., at various depths of soil, then weighing the residue, by removing the paper from the soil after two or three weeks.

Niklewski (8) added cellulose to the soil and determined the evolution of carbon dioxide as a result of the decomposition of cellulose. In addition to cellulose, 1 gm. K_2HPO_4, 1 gm. $MgSO_4$, 8 gm. $CaCO_3$ and $(NH_4)_2SO_4$ were added to 8 kgm. of soil. He found that the decomposition of cellulose in the soil is chiefly controlled by the presence of available nitrogen. The greater the amount of cellulose added to or present in the soil, the quicker will the nitrogen need set in. Nitrogen-fixing organisms were thought to play only a secondary rôle in normal soils, since cellulose is decomposed in those soils, without the addition of available nitrogen, only very slowly; this would not be the case, if nitrogen-fixing organisms were active. When only 0.125 per cent cellulose is added, there is already noticed a nitrogen need in a loess soil containing 0.15 per cent nitrogen. The greater the amount of cellulose added, the greater is the evolution of carbon dioxide up to a certain concentration, 1.5 per cent giving at first less carbon dioxide than 1.0 per cent cellulose. When the available nitrogen is lacking the curve soon falls to a certain level depending upon the rapidity of decomposition of the nitrogenous substances in the soil. The addition of 0.0125 per cent ammonium sulfate greatly stimulated cellulose decomposition. For 10 gm. of cellulose 1 gm. of $(NH_4)_2SO_4$ is used in the case of soil and 2 gm. in sand. Larger amounts of nitrogen acted injuriously, this injurious action may be later overcome.

On comparing the evolution of carbon dioxide with and without the addition of a nitrogen salt, Niklewski suggested the calculation of the available nitrogen in the soil; in the case of a loess soil containing 0.150 per cent nitrogen, 0.040 per cent was found to be active, while in the case of a sandy soil with 0.015 per cent, all the nitrogen was active.

Rahn (11) also found that when 0.5 to 1.0 per cent of straw is added to the soil, the available nitrogen is rapidly assimilated by the microörganisms using the straw as a source of energy, and a nitrogen-minimum ensues. When available nitrogen is added, the straw is rapidly transformed into substances with a constant carbon-nitrogen ratio.

Charpentier (3) added 1 per cent of cellulose, in the form of finely divided filter paper, to soil sieved through a 2-mm. sieve, and after carefully mixing the paper with the soil, the proper amount of moisture was introduced. At the end of the incubation period, the soil was air-dried and the amount of cellulose left was determined. Stable manure was found to have a decided stimulating effect upon the decomposition of cellulose in the soil, especially when the moisture content is satisfactory. The influence of reaction is not of great importance in the decomposition of cellulose. The favorable influence of manure is due to the nutrients present, especially the nitrogen. The greater the amount of nutrients (nitrogen and minerals) present in the manure, the greater is its action. The poorer the soil is, the greater is the influence of the manure. When ammonium sulfate and manure containing the same amount of nitrogen are added to the soil, the stimulating effect upon cellulose decomposition was found to be the same. These results were confirmed by Barthel and Bengtsson (2).

A study of the literature on the subject of cellulose decomposition in the soil as an index of microbiological activities would, therefore, lead us to assume that we are dealing here more with a function indicating the physical and chemical condition of the soil, especially the available nitrogen, rather than the specific microbial flora. This can be found to hold true, to some extent at least, after a careful theoretical consideration of the subject.

Cellulose is decomposed in the soil by fungi, actinomycetes and bacteria, including aerobic and anaerobic forms, thermophilic and denitrifying organisms. Probably all soils contain some, if not all, of these groups capable of decomposing cellulose. When cellulose is added to the soil, one of these groups will be favored more than the others, depending upon the physical and chemical condition of the soil, especially reaction, aeration, moisture content, and the presence of available nitrogenous substances. Bacteria which decompose cellulose are incapable of assimilating atmospheric nitrogen and have to depend upon fixed available compounds for their nitrogen supply. Whether nitrogen-fixing bacteria are capable of utilizing the intermediary products of cellulose decomposition, as found by Pringsheim (9) and others, is another point and need not concern us here. It is sufficient to say that cellulose offers a readily available source of energy for organisms capable of utilizing it, and these will do it only in the presence of available nitrogen and mineral salts. It has been found in this laboratory[2] that there is a definite relation between the amount of cellulose decomposed and nitrogen assimilated by an organism, especially in the case of fungi, which were studied most extensively; this ratio was found to be, for these organisms, 30 to 1; i.e., about 30 parts of cellulose are decomposed for every part of nitrogen assimilated, either from ammonium sulfate or sodium nitrate. This ratio will probably be found to be wider for bacteria and actinomycetes, since these organisms produce a relatively much smaller amount of growth than the fungi. In view of this definite relation, the available nitrogen becomes the controlling factor. It remains to be seen whether there is, in normal soils, a different relation between the cellulose decomposition and the amount of nitrogen available, because of the mixed microflora.

METHODS

The determination of cellulose decomposition in the soil can be carried out by two methods: (a) Measuring the evolution of carbon dioxide as a result of decomposition of cellulose, as suggested by Niklewski (8), Dvorak (6) and Rahn (10, 11) and as reported in detail elsewhere (16); and (b) according to the method of Charpentier (3) and Barthel and Bengtsson (2). The second method is carried out as follows:

Preparation of Schweitzer's reagent. Two hundred grams of copper sulfate are dissolved in hot water and precipitated with a calculated amount of ammonia (95 cc. of ammonia, sp. gr. 90). The excess of ammonia is then neutralized with sulfuric acid. The precipitate is washed by decantation in a large bottle three or four times and is then transferred to a Büchner funnel and filtered through hardened filter paper by the use of suction. With the aid of a porcelain spoon the excess of water is pressed out from the copper hydroxide. It is then removed in the form of a hardened paste from the filter paper and introduced into a bottle containing ammonia water and shaken in a shaking machine for 4–5 hours. An undissolved

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[2] Results to be published later.

part of the copper hydroxide should remain at the bottom of the flask. The Schweitzer's reagent prepared in this way should contain 1.5 gm. of copper per 100 cc. of solution.

To test the strength of the reagent, 5 cc. are placed in a crucible of constant weight, near a dish of H_2SO_4 under a bell-jar. As soon as all the ammonia is absorbed, the $Cu(OH)_2$ is dried and heated to constant weight and weighed as CuO.

Process of cellulose determination. Cellulose is added to the soil either in the form of finely cut or well ground filter paper. After the soil is properly mixed, a 20-gm. sample is obtained from moist, or preferably air-dried, soil. The sample is placed in a 250-cc. sampling bottle, 100 cc. of the Schweitzer's reagent is added; the bottle is then stoppered with a rubber stopper and shaken for an hour in a shaking machine. After settling, somewhat more than 50 cc. of the liquid is filtered through a Gooch crucible by the use of suction. Fifty cubic centimeters of the filtrate are then precipitated with 200 cc. of 80 per cent alcohol and the precipitate is filtered through a Gooch crucible and washed as follows: (1) dilute 1 per cent HCl, (2) warm distilled water, (3) dilute 2 per cent KOH to get rid of humic acids—washing with KOH is continued until all brown color disappears, (4) warm distilled water, (5) dilute 1 per cent HCl to get rid of free alkali, (6) warm distilled water until free from chlorides, (7) alcohol—after cooling the crucible, (8) ether.

Dry to constant weight at 110° C., weigh, burn off and weigh again. The difference between the two weights gives the quantity of cellulose for 10 gm. of the sample.

Before the cellulose-decomposing power of the soil could be tested and compared with the crop productivity of the soil, some information had to be gained on a proper incubation period to be used, on the influence of air-drying of soil and the addition of available nitrogen upon cellulose decomposition. The temperature of incubation was always 25°–28°C. while the moisture content was 60 per cent of the maximum moisture-holding capacity of the soil. The soil used in the preliminary experiments was a sassafras gravelly loam with a pH value of 6.2 and average fertility characteristic of this series.

The influence of the amount of cellulose added and period of incubation upon the decomposition of cellulose in the soil previously air-dried is shown in table 1. In all cases, the substances extracted by ammoniacal copper solution and precipitated with alcohol were determined in the control soil, to which no cellulose had been added. The weight of these substances was subtracted from the weight of the cellulose determined in the treated soil. The studies were all done in duplicate, and the averages only are given, since a fair check was obtained in the majority of cases.

There is a decided increase in the actual amount of cellulose decomposed with the increase in the amount of cellulose added to the soil. However, the per cent of cellulose decomposed decreases with the increase in the concentration of cellulose, especially when the amount of cellulose added is large. This is particularly true when the cellulose is added directly to fresh soil and not to air-dried soil, which was used in the previous experiment.

Table 2 shows the influence of air-drying and the addition of an available source of nitrogen upon cellulose decomposition in the soil. In this case the same sample of fresh soil was divided into two portions, one-half of which was kept moist and one-half air-dried, for two weeks. At the end of that period of time, 100-gm. portions of the moist and air-dried soils were placed in

tumblers, 1 gm. of finely divided filter paper was added to each, the soil and cellulose were well mixed, the proper amount of moisture added, tumblers covered with glass plates and placed in the incubator for twenty-one days. To some of the tumblers 50 mgm. of ammonium sulfate were added. The results are given in table 2.

Air-drying exerts a decided stimulating effect upon the decomposition of cellulose. This is due to the fact that air-drying followed by moistening of soil brings about a greater availability of the soil nitrogen. In this particular experiment, 100-gm. portions of the air-dry and moist soils were incubated

TABLE 1

Influence of cellulose concentration and period of incubation on cellulose decomposition

CELLULOSE ADDED PER 100 GM. OF SOIL	INCUBATION	CELLULOSE DECOMPOSED	
gm.	*days*	*gm.*	*per cent*
0.25	7	0.089	35.4
	18	0.168	67.1
	32	0.200	80.0
0.50	7	0.141	28.2
	18	0.293	58.6
	32	0.411	82.2
1.00	7	0.230	23.0
	18	0.547	54.7
	32	0.663	66.3

TABLE 2

Influence of air-drying and addition of available nitrogen upon cellulose decomposition in the soil.

SOIL TREATMENT	CELLULOSE DECOM- POSED IN 21 DAYS
	per cent
Fresh moist soil...	24.0
Soil air-dried 14 days...	34.9
Moist soil + 50 mgm. $(NH_4)_2SO_4$.................................	82.9
Air dry soil + 50 mgm. $(NH_4)_2SO_4$...............................	83.8

separately, without the addition of any cellulose. It was found that, at the end of the 21-day period of incubation, the soil that was previously air-dried contained 2.9 mgm. of inorganic nitrogen (as ammonia and nitrate) more than the soil kept constantly moist. The actual quantities of cellulose decomposed, as reported in table 2, are less than those reported in table 1. This is undoubtedly due to the fact that the soil used in the first experiment (table 1) was air-dried for a considerable period of time and, as shown by Waksman and Starkey (14), the greater the period of air-drying of a soil, the greater is the increase in the decomposition of the soil organic matter, when the soil is moistened, resulting in an increase in available nitrogen.

These results tend to confirm those of Christensen (5), Niklewski (8), Charpentier (3) and Barthel and Bengtsson (2), that the amount of cellulose decomposed in the soil is a result of the concentration of available nitrogen. Even where 50 mgm. $(NH_4)_2SO_4$ has been added to 100 gm. of soil and 1 gm. of filter paper, no ammonia or nitrate nitrogen could be detected at the end of the experiment, showing that all the nitrogen had been assimilated by microorganisms and probably converted into microbial protein.

To learn what groups of organisms are stimulated most by the addition of cellulose to the soil, 1-gm. portions of filter paper were added to 100-gm. portions of three differently treated soils and placed in tumblers; to some of the tumblers, 100 mgm. of $NaNO_3$ was added. The proper amount of moisture was then added to each soil and tumblers covered and incubated for seventeen days. At the end of that period, the fungi, actinomycetes and

TABLE 3

Influence of 1 per cent of cellulose, with and without $NaNO_3$, upon the development of microorganisms in the soil

SOIL NUMBER	TREATMENT	REACTION	NaNO₃ ADDED PER 100 GM. OF SOIL	FUNGI		BACTERIA		ACTINOMYCETES	
				No cellulose	Cellulose added	No cellulose	Cellulose added	No cellulose	Cellulose added
		pH	*mgm.*	*thousands*	*thousands*	*thousands*	*thousands*	*thousands*	*thousands*
5A	Manured, unlimed	5.5	0	87.3	320	6,500	21,920	1,800	6,400
		5.5	100	87.3	3,100	6,500	40,400	1,800	4,600
7A	Unmanured, unlimed	5.1	0	115.7	160	3,900	3,600	1,260	600
		5.1	100	115.7	4,800	3,900	2,480	1,260	400
7B	Unmanured, limed	6.5	0	25.4	47	7,700	17,400	2,760	2,200
		6.5	100	25.4	290	7,700	47,000	2,760	3,200

bacteria were determined by the plate method, described elsewhere (12). The results are given in table 3. The amounts of cellulose decomposed in these soils are found in table 9.

The largest amount of cellulose was decomposed in 5A to which nitrogen in the form of $NaNO_3$ was added (818.5 mgm.), followed by 7B + $NaNO_3$ (535.8 mgm.) and 7A + $NaNO_3$ (270.7 mgm.); considerably smaller amounts of cellulose were decomposed when no $NaNO_3$ was added, as shown in table 9 where the results on cellulose decomposition obtained in this experiment are reported.

It is thus found that the addition of cellulose to the soil greatly stimulates the development of fungi and bacteria and to a lesser extent of actinomycetes. The relative stimulation depends, however, on the nature of the soil. In the case of the heavily manured but acid soil (5A), the addition of 1 per cent of cellulose brought about the same relative increase in the numbers of bacteria,

fungi and actinomycetes; the amount of cellulose decomposed, without the addition of available nitrogen, was only about 0.1 of a gram. However, when nitrogen was added, in the form of $NaNO_3$ (100 mgm.), the amount of cellulose decomposed increased six to seven times, the number of fungi increased ten times, the number of bacteria increased two-fold and the number of actinomycetes was even less than where no nitrogen has been added.

In the case of the exhausted acid soil (7A), the addition of cellulose without any available nitrogen brought about a slight increase in the number of fungi, no perceptible change in the number of bacteria and even a decrease in the number of actinomycetes. The amount of cellulose decomposed, as indicated by the evolution of carbon dioxide, was very small. But when 100 mgm. of $NaNO_3$ was added, the number of fungi increased thirty times, while the bacteria and actinomycetes not only did not increase but even decreased. In this case all the cellulose decomposed (270.7 mgm.) was due to the activities of fungi. The fact that no greater amount of cellulose was decomposed in this soil may be due either to the absence, in this soil, of available minerals, notably phosphates, or to the lack of activity of the bacteria and actinomycetes, possibly due to the acidity of the soil (pH = 5.0). The addition of cellulose to the limed unfertilized soil (7B), which is favorable for the development of bacteria and unfavorable for fungi, due to the reaction of the soil (pH = 6.4), brought a slight increase in the number of fungi and an appreciable increase in the number of bacteria; when nitrogen was added, the increases in the numbers of both groups of organisms were even more marked. The actinomycetes were hardly affected.

This experiment indicates that, in slightly acid soils, the fungi may be most concerned with the decomposition of cellulose, while in limed, neutral or slightly acid soils, both fungi and bacteria play an active part. The lack of development of actinomycetes may be due to the short period of incubation used, since these organisms develop only very slowly.

The fungi produce an abundant growth in the soil and require a minimum amount of nitrogen (3–8 per cent) for the synthesis of their protoplasm. In the absence of the available nitrogen, the fungi, as well as the cellulose decomposing actinomycetes and bacteria, will develop only to a limited extent, and, therefore, will decompose only a limited amount of cellulose.

It was shown by Pringsheim (9), Dvorak (5) and others that Azotobacter is capable of fixing nitrogen using cellulose or its decomposition products as a source of energy. This process seems to be a rather slow one, otherwise nitrogen would not become the limiting factor in cellulose decomposition.

A detailed study of the influence of available nitrogen on cellulose decomposition will be reported elsewhere, here we may merely cite a typical experiment (table 4), using 1 gm. of cellulose in 100 gm. of soil and incubating for 6 weeks.

The addition of a small amount of nitrogen stimulated cellulose decomposition in the fertile soil to a greater extent than in the unfertile soil. This again may be due to the difference in available minerals or in the microflora.

When we come to compare the difference in soil fertility, using the power of cellulose decomposition as an index, we must keep in mind the fact that the soils will vary in their nitrogen content and in the rapidity with which the nitrogen becomes available, as indicated by the process of nitrification (13). If two soils vary in the available nitrogen, we would, therefore, expect that, *ipse facto*, they should also vary in the amount of cellulose decomposed, outside of any differences in their microbial flora.

The same series of nitrogen plots that was used in the previous studies reported in this series of papers dealing with the methods of determining the microbiological condition of the soil, were also used in these experiments. Soils 5A and 5B received yearly applications of 32 tons of cow manure and minerals

TABLE 4

The influence of available nitrogen, as $NaNO_3$, upon cellulose decomposition in the soil

NaNO₃ PER 100 GM. OF SOIL	CELLULOSE DECOMPOSED	
	Unfertile soil (7A), 6 weeks incubation	Fertile soil (5A), 4 weeks incubation
mgm.	*per cent*	*per cent*
0	36.9	42.2
25	41.7	66.7
100	59.7	97.2

TABLE 5

Cellulose decomposition in soils of different fertility

PLOT NUMBER	SOIL REACTION	NITRATE NITROGEN IN 100 GM. ORIGINAL SOIL	CELLULOSE DECOMPOSED
	pH	*mgm.*	*per cent*
5A	5.4	0.17	64.5
5B	6.7	0.20	72.8
7A	5.0	0.04	31.9
7B	6.4	0.04	50.9
9A	5.6	0.09	55.3
11A	4.4	0.08	52.7

(640 pounds of acid phosphate and 320 pounds of potassium chloride) per acre; soils 7A and 7B received no fertilizer; soils 19A and 19B, minerals only; soil 9A, 320 pounds $NaNO_3$ and minerals; 11A and 11B, $(NH_4)_2SO_4$ equivalent in nitrogen to 320 pounds $NaNO_3$ and minerals. In addition, all the B plots received two tons $CaCO_3$ every five years.

The first samples were taken December 6, 1922, when the soil was frozen. After allowing the soil to thaw off, the excess of water was evaporated by exposure to the air for 48 hours, 0.5 per cent of cellulose was added to 100-gm. portions of the soil (on a dry basis,) and the mixed soil was placed in tumblers, covered with glass and incubated for 6 weeks at optimum moisture. The amounts of cellulose decomposed as well as the amounts of nitrate nitrogen originally present in the soil are given in table 5.

The results presented in table 5 show that there is a certain parallelism between the cellulose-decomposing power of differently treated soils and the available nitrogen in those soils, as shown by their nitrate content. No correlation at all is found between the soil reaction and cellulose decomposition. Similar results were also obtained by Christensen (5), Charpentier (3), and Barthel and Bengtsson (2).

To demonstrate definitely whether the differences obtained in the amounts of cellulose decomposed in the soils taken from plots of different fertility is due to the differences in the nitrogen availability in the particular soils or to the differences in the microbiological flora brought about by the continued treatment of the soil, the plots were again sampled on June 26, 1923. The soils were tested in two ways for their cellulose-decomposing power: (1) by

TABLE 6

Influence of soil treatment and addition of available nitrogen upon cellulose decomposition in the soil*

PLOT NUMBER	SOIL REACTION	NO₃-N IN 100 GM. OF SOIL†	CELLULOSE DECOMPOSED	
			No nitrogen added	50 mgm. NaNO₃ per 100 gm. of soil
	pH	*mgm.*	*per cent*	*per cent*
5A	5.6	1.70	35.5	79.1
5B	6.8	2.90	53.6	77.7
7A	4.8	0.52	13.1	45.7
7B	6.8	1.02	37.2	80.9
11A	4.2	0.75	46.6	88.9
11B	6.2	1.60	36.5	86.6
19A	5.2	0.60	22.4	69.5
19B	6.5	1.80	52.2	85.6

* 1 per cent filter paper (about 94 per cent pure cellulose), period of incubation 30 days.

† Nitrate-nitrogen accumulated in the same soils, incubated under the same conditions, but without the cellulose.

adding cellulose (1 per cent filter paper), with and without available nitrogen, to the soil and (2) by adding a small amount of soil (1 gm.) to 100 gm. of sterile sand, containing 1 gm. of filter paper and the necessary mineral nutrients. The nitrate nitrogen was determined in control soils incubated with the same amount of moisture for the same period of time, but without the addition of cellulose. The results are given in tables 6 and 7.

The results speak for themselves. When no available nitrogen is added to the soil together with the cellulose, there is found a decided difference in the cellulose-decomposing power of fresh soils taken from variously treated plots, in which differences in fertility have been established. The differences correspond, however, to a large extent, to the available nitrogen in the soil as indicated by their nitrate content, with but one exception, namely 11A. This soil which has been receiving yearly applications of minerals and am-

monium sulfate has been made so acid that the nitrifying capacity has been injured. Some of the available nitrogen is probably present in the form of absorbed ammonium compounds which are readily utilized as a source of nitrogen by the cellulose-decomposing microörganisms.

There is no correlation between the reaction of the soil and its cellulose-decomposing capacity, since the fungi which take a very active part in the decomposition of cellulose in the soil will thrive readily even under the most acid reactions in which cultivated plants will barely grow at all.

To test the cellulose-decomposing activities of the microbiological population of the different soils, 1 gm. of the variously treated soils was added to 100 gm. of sterile sand containing 1 per cent of filter paper and 20 cc. of a mineral solution (containing 10 gm. of $(NH_4)_2SO_4$, 3 gm. K_2HPO_4, 2.0 gm. $MgSO \cdot 7H_2O$ and 1.0 gm. NaCl in 1000 cc. of distilled water) and placed in 250-cc. Erlenmeyer flasks; these were incubated for 21 days. The amount of cellulose decomposed was found to be practically the same for all soils, since all of them harbor organisms capable of decomposing cellulose. Under

TABLE 7

Decomposition of cellulose in sand by 1 gm. portions of variously treated soils

PLOT NUMBER	CELLULOSE DECOMPOSED
	per cent
5A	92.8
5B	91.7
7A	94.9
7B	96.1
11A	93.6
11B	92.0

optimum conditions, these organisms will all develop rapidly and decompose the cellulose, as shown in table 7. This method can, therefore, be only qualitative in nature.

To bring out more definitely the influence of addition of available nitrogen and period of incubation upon the amount of cellulose decomposed, another set of samples, taken September 29, 1923, were placed, in 100-gm. portions, in tumblers. One gram of finely cut filter paper was added to each and well mixed with the soil; 100 mgm. of $NaNO_3$ was added to some of the tumblers; the soils were brought to optimum moisture, the tumblers covered and incubated at 25–28°. The results are given in table 8.

The results indicate that a certain differentiation between the cellulose-decomposing capacity of differently treated soils is found, when a long period of incubation (42 days) is used and no available nitrogen is added; when some available nitrogen is added to the soil, a short period (14–15 days) of incubation is required. When no available nitrogen is added, the differences in cellulose decomposition are due to a large extent to the available nitrogen in the soil; when available nitrogen is added, the differences in cellulose de-

composition are either due to the presence or absence of other chemical elements in the soil, such as phosphates, or to differences in the microbiological activities in the different soils.

Niklewski (8) suggested using the evolution of carbon dioxide as an index of cellulose decomposition in the soil. To compare the evolution of carbon dioxide with the decomposition of cellulose as influenced by the available nitrogen and soil microflora, soils 5A, 7A and 7B were used: the first (5A) is heavily manured, has a pH value of 5.5 and is rich in microörganisms; the second (7A) is unfertilized, has a pH value of 5.0–5.1, is rich in fungi and low in bacteria; the third (7B) is unfertilized but limed, has a pH value of 6.5, is rich in bacteria and poor in fungi. One gram of filter paper was added to 100 gm. of soil and well mixed; the soil was then placed in an apparatus described elsewhere (15), the proper amount of moisture was then added, and the evolution of carbon dioxide measured at frequent intervals. After 17

TABLE 8

Influence of period of incubation and presence of available nitrogen on cellulose decomposition

PLOT NUMBER	NO NITROGEN ADDED		100 MGM. NaNO₃ ADDED
	Cellulose decomposed		Cellulose decomposed in 14 days
	In 14 days	In 42 days	
	per cent	*per cent*	*per cent*
5A	18.4	33.8	87.8
7A	6.7		30.5
9A	18.7		79.4
19A	18.7	16.2	58.5
5B	16.5	24.9	72.6
7B	11.8	9.2	60.1
11B	16.1		79.4
19B		16.5	64.7

days of incubation, the nitrate and cellulose were determined in the soil. The results are given in table 9. The changes in the number of microörganisms, as a result of addition of cellulose, with and without NaNO₃, to these soils, are recorded in table 3.

The results show definitely that both the evolution of carbon dioxide and the determination of residual cellulose can serve as measures of the power of the soil to decompose cellulose and that the decomposition of cellulose may serve to some extent as an index both of the available nitrogen in the soil and of the activities of the microbiological flora. When no soluble nitrogen was added, the amounts of cellulose decomposed run parallel to the amounts of nitrate that will accumulate in the soil; thus serving as an index of the availability of the soil nitrogen. But decided differences are obtained even when sufficient available nitrogen is added. These differences may be due to the differences in the microbiological activities of the different soils, as

pointed out above. Of course we must consider, in addition to the influence of available nitrogen, also the influence of available minerals, especially potassium salts and phosphates, as well as $CaCO_3$ upon the decomposition of cellulose in the soil. To eliminate this factor, the following method, similar to that of Niklewski (8) was finally adopted:

Two hundred milligrams $CaCO_3$, 50 mgm. K_2HPO_4, 25 mgm. $MgSO_4$ and 1 gm. of finely cut filter paper were added to each 100-gm. portion of soil and well mixed in. The soil was then placed in the apparatus used for the evolution of carbon dioxide and enough water added to bring the moisture content to optimum. Two flasks were used for every soil. The amount of CO_2 evolved from the same soils to which the $CaCO_3$ and minerals were added, but not the cellulose, was also determined. The results of a typical experiment are given in table 10.

TABLE 9

Influence of addition of available nitrogen upon cellulose decomposition in different soils*

| SOIL NUMBER | NaNO₃ ADDED TO 100 GM. SOIL | NO₃-N* USED UP | EVOLUTION OF CO₂ | | | CELLULOSE DECOMPOSED IN 100 GM. OF SOIL |
			In soil + cellulose	In soil alone	Due to addition of cellulose	
	mgm.	*mgm.*	*mgm.*	*mgm.*	*mgm*	*mgm.*
5A	0	3.50	282.70	72.97	209.73	109.7
5A	100	17.90	712.80	72.88	639.92	792.5
7A	0	0.95	72.60	22.24	50.36	47.8
7A	100	6.65	171.05	22.24	148.81	189.7
7B	0	1.20	142.45	57.83	84.62	
7B	100	10.50	429.55	58.82	371.73	454.8

* Nitrate formed in soil was determined in separate portions to which no cellulose has been added; nitrate-nitrogen used up was obtained by subtracting the residual nitrates from that formed in the control soil + the added nitrate, per 100 gm. of soil. Period of incubation was 17 days.

TABLE 10

Decomposition of cellulose in various soils as indicated by the evolution of CO_2 and amount of cellulose left

| SOIL NUMBER | FINAL REACTION | NITRATE-N ACCUMULATION IN 100 GM. SOIL WITHOUT CELLULOSE | EVOLUTION OF CO₂ IN 21 DAYS | | | CELLULOSE DECOMPOSED IN 100 GM. OF SOIL |
			Soil + cellulose	Soil alone	Due to addition of cellulose	
	pH	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*
5A	6.7	2.9	764.10	107.22	656.88	451
5B	6.9	1.4	544.50	67.65	476.85	418
7A	6.5	0.7	540.40	127.05	413.35	310
9A	6.4	1.5	417.80	132.00	285.80	213
11A	6.0	2.3	692.60	156.75	535.85	407
11B	6.8	1.2	424.00	82.50	341.50	210

The addition of $CaCO_3$ and minerals to the soil brings about a greater evolution of carbon dioxide in the acid than in the limed plots (*B*). This is probably partly due to the chemical liberation of carbon dioxide by the

interaction of organic and inorganic substances and $CaCO_3$. It may also be due to improvement in the physical condition of the acid soils by the calcium carbonate and stimulation of activities of bacteria. The greatest amounts of cellulose were decomposed, as shown by the residual cellulose, in the manured soils (5A and 5B), followed closely by the ammonium sulfate soil (11A). Although 11A contained almost twice as much available nitrogen (as nitrate) than 5B, the amount of carbon dioxide produced from 11A was only slightly greater than from 5B, while the total amount of cellulose decomposed was actually smaller. This is probably due to the fact that the fungi which are more active in 11A, require more nitrogen for every unit of cellulose decomposed than the bacteria, which are more active in 5B. The sodium nitrate soil (9A) and limed, ammonium sulfate soil (11B) gave the smallest amounts of cellulose decomposed, both by measuring the residual cellulose and the carbon dioxide evolved, less so than the unfertilized soil 7A. This again points to the fact that the available nitrogen, although a very impor-

TABLE 11

Influence of $NaNO_3$ upon the decomposition of cellulose, in the presence of $CaCO_3$ and minerals

SOIL NUMBER	NaNO₃ ADDED TO 100 GM. OF SOIL	EVOLUTION OF CO₂ IN 14 DAYS			CELLULOSE DECOMPOSED IN 100 GM. OF SOIL
		Soil + cellulose	Soil alone	Due to addition of cellulose	
	mgm.	*mgm.*	*mgm.*	*mgm.*	*mgm*
5A	0	544.50	75.50	469.00	3.7
5A	25	778.25	75.50	702.75	567
5A	50	817.30	75.50	741.80	6.0
7A	0	364.10	88.60	275.50	222
7A	25	526.35	88.60	437.75	437
7A	50	684.20	88.60	595.60	557

tant factor affecting the amount of cellulose that can be decomposed in a given soil and in the rapidity of decomposition of the cellulose, may not be the only factor concerned. When sufficient calcium carbonate and minerals are added to the soil, the amount of cellulose decomposed can serve in a way as an index of the nitrogen of the soil that can become available, if sufficient lime and minerals are added.

To test this point further, six 100 gm. portions of soil 5A and of soil 7A were placed in the respiratory flasks; 200 mgm. $CaCO_3$, 50 mgm. K_2HPO_4, 25 mgm. $MgSO_4$ and 1 gm. of finely divided filter paper were added to each flask. Two flasks from each group received no nitrogen; two received 25 mgm. $NaNO_3$ and two received 50 mgm. $NaNO_3$. The amount of carbon dioxide evolved during the 14-day incubation period and the amounts of cellulose decomposed were determined. The results are given in table 11.

The results presented in table 11 help to establish further the fact that there is a definite correlation between the available nitrogen present in the soil and the amount of cellulose decomposed, whether this is measured by the

evolution of carbon dioxide or by the amount of residual cellulose. The addition of 25 mgm. of $NaNO_3$ resulted in a proportionally much greater increase in the amount of cellulose decomposed than the addition of 50 mgm. of $NaNO_3$. The addition of 25 mgm. $NaNO_3$, or about 4 mgm. of available nitrogen, resulted in an increase of the amount of cellulose decomposed in 5A by 180 mgm., in other words, for every milligram of available nitrogen, there was an increase of 45 mgm. of cellulose decomposed. This ratio is found to be 54 to 1 in the case of 7A. It was pointed out elsewhere, that pure cultures of fungi will decompose about 30 mgm. of cellulose for every
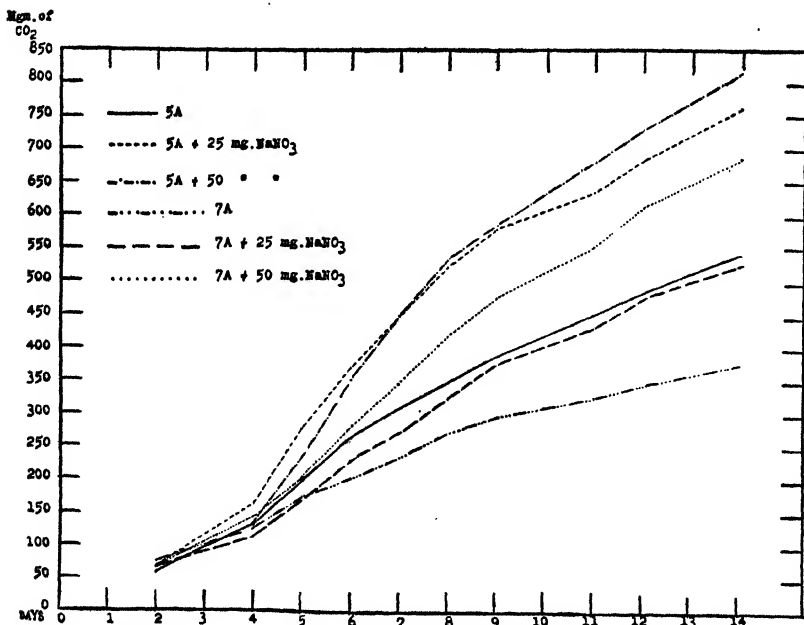
Fig. 1. Influence on $NaNO_2$ upon the Course of Decomposition of Cellulose as Indicated by the Evolution of Carbon Dioxide

1 mgm. of nitrogen assimilated. In view of the fact that the bacteria require a much smaller amount of nitrogen for the synthesis of their protoplasm for the same amount of energy used up, the wider ratio between the amount of cellulose decomposed and nitrogen assimilated (45 to 54:1) is due to the activities of bacteria, in addition to the fungi; this is especially true, since these soils have been treated with calcium carbonate which has made the reaction favorable for the development of the bacteria. The influence of available nitrogen upon the course of cellulose decomposition, as indicated by the evolution of carbon dioxide is given in figure 1.

It is interesting to compare the influence of nitrogen upon cellulose decomposition in untreated soil and in soil to which a small amount of $CaCO_3$ (0.2 per cent), K_2HPO_4 (0.05 per cent) and $MgSO_4$ (0.025 per cent) have been added; this can be done by comparing the results in tables 4 and 11. When no lime and minerals are added to an infertile acid soil (7A—table 4), the addition of 25 mgm. of $NaNO_3$ brought about an increase of only about 5 per cent in the amount of cellulose decomposed, while the addition of 100 mgm. $NaNO_3$ resulted in an increase of 23 per cent cellulose decomposed; in the case of the fertile soil (5A—table 4), the addition of 25 mgm. $NaNO_3$ brought about an increase of 24.5 per cent in the amount of cellulose decomposed and 100 mgm. $NaNO_3$, of 55 per cent. This shows definitely that although nitrogen is an important factor, there is still something in 5A, which makes this soil far more active, from a microbiological view point. This may be due to the greater abundance of minerals and buffering substances, which make soil 5A decompose cellulose much more actively than 7A. When lime and minerals are added to these two soils (table 11) the addition of 25 mgm. $NaNO_3$ brought an increase of cellulose decomposition of 21.5 per cent in the unfertile soil (7A) and only 18 per cent in the fertile soil (5A); 50 mgm. $NaNO_3$ brought about an increase in the amount of cellulose decomposed by 33.5 per cent in 7A and by 29 per cent in 5A. In other words, when lime and minerals are added to two soils, one of which is very fertile and one very infertile, the addition of nitrogen stimulates cellulose decomposition about alike in both soils. But when no lime and minerals are added, the addition of available nitrogen will stimulate cellulose decomposition to a much greater extent in the fertile than in the infertile soil.

SUMMARY

The results brought out in this paper indicate that the determination of the power of a soil to decompose cellulose can be added to the group of methods used for carrying out a microbiological analysis of a soil. A study of the processes of nitrification brought out that the information obtained by this method can serve both as a basis for determining the microbiological condition of the soil, the rapidity with which the soil nitrogen becomes available, as well as the soil reaction and the buffer content of the soil. In a similar manner, the determination of the power of a soil to decompose cellulose can yield information on the microbiological condition of the soil as well as on its available nitrogen.

For every milligram of nitrogen that is available or that can become available in the soil, in the particular period of time, there will be decomposed approximately 40 to 50 mgm. of cellulose in the given amount of soil.

A study of the cellulose-decomposing power of the soil, both without and with the addition of a small amount of available nitrogen, can thus yield information for the differentiation of soil fertility, just as the determination

of numbers of microörganisms, of the nitrifying capacity and of the respiratory power of the soils. This method can supply information on the total available nitrogen in the soil as well as on the differences in the activities of the soil microörganisms. The results obtained by means of this method, when added to those obtained by the other methods, allow us to look forward towards having as complete a picture as possible of the microbiological processes in the soil and the chemical and physical condition of the soil, which affect these processes and which together go to make up soil fertility.

To measure the cellulose-decomposing power of the soil, three methods are recommended:

1. One gram of finely cut or well ground filter paper is well mixed with 100 gm. of fresh sieved soil; this is then placed in a tumbler, brought to optimum moisture, covered and incubated for 42 days, at 25–28°C, with frequent additions of water to keep the soil at optimum moisture. The amount of residual cellulose is determined in the soil, which is first air dried, by the method developed by Charpentier. The residual cellulose is then subtracted from the amount of cellulose originally present in the soil, determined by extracting 20 gm. of the original soil and 200 mgm. of the original paper, giving the amount of cellulose actually decomposed in the soil.

2. One gram of well ground filter paper and 100 mgm. of sodium nitrate are added to 100 gm. of soil, which is then well mixed and placed in a tumbler, brought to optimum moisture, covered and incubated for fifteen days. The amount of cellulose decomposed is determined in a manner similar to that used in the first method.

3. One hundred grams of soil, two hundred mgm. $CaCO_3$, 50 mgm. K_2HPO_4, and 25 mgm. $MgSO_4$, with and without 1 gm. of cut or ground filter paper, is placed in a respiratory apparatus and the amount of carbon-dioxide given off determined for fourteen days. The excess of carbon dioxide produced and the amount of cellulose decomposed in the soil containing cellulose, over the soil containing the minerals only, will serve as an index of cellulose decomposition and, *ipse facto*, of the available nitrogen in the soil. For every milligram of nitrogen that is available in the soil or that can become available in the given period of time, 40 to 50 mgm. of cellulose will be decomposed.

Every one of these three methods yields information on the cellulose-decomposing power of the soil viewed for a different angle. The first method, or the determination of cellulose decomposition in the untreated soil, supplies us with information as to the available nitrogen in the soil, when not treated further. The second method, or the determination of rapidity of cellulose decomposition in the soil, in the presence of available nitrogen, supplies information on the physical and chemical condition of the soil bearing upon microbiological activities and soil fertility, outside of the nitrogen factor: the addition of nitrogen will bring about greater decomposition of cellulose in the more fertile soil, with a more active microbiological flora. The third method, namely the determination of the cellulose decomposing capacity of the soil, in the presence of $CaCO_3$, K_2HPO_4 and $MgSO_4$, the lack of which may become limiting factors to cellulose decomposition, supplies information on the nitrogen of the soil which can become available, when the soil is properly limed and the necessary amount of mineral elements is added.

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SOME OBSERVATIONS ON THE DECOMPOSITION OF ORGANIC MATTER IN SOILS[1]

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INTRODUCTION

The carbon dioxide evolved from pure and mixed cultures of microörganisms in artificial and soil media has frequently been used to measure microbiological activity and decomposition of organic matter. Production of carbon dioxide, however, is seldom an absolute index of these processes. When the decomposition of organic matter is measured by the amount of CO_2 produced, it should be kept in mind that the CO_2 is not the only product formed from the carbon of the organic matter in the process. The autotrophic microörganisms reassimilate some of the CO_2 while all heterotrophic organisms reassimilate some of the carbon during the process of growth and reproduction before it has completely decomposed; the fungi reassimilate much more carbon than the bacteria per unit of organic matter decomposed. Carbon dioxide is also not the only carbonaceous product of decomposition of organic matter even under aerobic soil conditions, since various intermediate products may be formed, while some of the constituents of the organic matter may be more resistant to decomposition than others. In general, however, the incomplete decomposition products of some organisms are further attacked by others and sooner or later appear as CO_2. The work of Bail (2), Neller (16) and Potter and Snyder (19) clearly show that cultures of bacteria, fungi and yeasts used in mixtures as well as the whole soil infusion produced much more CO_2 from sterilized organic matter than do any pure cultures of microörganisms.

Apparently the autotrophic microörganisms make up a small portion of the total numbers of microörganisms in the soil and it is undoubtedly true that, in the presence of an abundant and varied flora and under aerobic conditions, the organic matter undergoes relatively complete oxidation and only comparatively small amounts of incomplete oxidation products are

formed and accumulate. The CO_2 produced from soils should, therefore, give a reliable although not an absolute index of the decomposition of organic matter. With this in mind, in considering later the amounts of organic materials decomposed, we shall be able to realize that the recorded results on CO_2 production are lower than the actual amounts of organic matter decomposed.

HISTORICAL

Source of soil organic matter. The organic matter in soils is largely replenished by the whole plants where they are not removed, roots and stubble from cut crops and organic manures added to the soil. Plant residues left in the soil may amount to 10–50 per cent of the organic matter removed in the cut crops [van Suchtelen (24)].

Relative ease of decomposition of certain materials and some factors involved. Wollny's extensive fundamental work (30) is still outstanding among the contributions on the decomposition of organic matter. Wollny found that the amounts of nitrogen contained in the organic materials greatly affect their rapidity of decomposition. Materials poor in nitrogen and rich in cellulose (cereal straws) decomposed more slowly than those rich in nitrogen but poor in cellulose (legume straws). Bone, guano, meat and bird excrements decomposed most quickly; the straws used for fertilizers and litters come next; then were listed the more common barnyard manures; hides, hoofs, and forest litters decomposed with difficulty; peat was the most resistant of all those studied.

Dvořák (4) stated that materials rich in oxygen and poor in carbon decomposed more quickly than those rich in carbon and poor in oxygen. He observed the following percentage decomposition of certain substances, as measured by the carbon dioxide produced in twenty-one days from 10 gm. of material added to 100 gm. of soil:

	per cent		per cent
Clover	59.7	Oak leaves	17.7
Glucose	42.1	Wheat straw	14.5
Rice straw	29.0	Cellulose	11.8
Levulose	27.2		

The rates of decomposition of these substances were likewise distinctive.

Fraps (5) reported that cottonseed meal, corn chops, rice hulls, and wheat shorts decomposed more rapidly (72–81 per cent in 14 weeks) than meat, blood and tankage (47–68 per cent in 14 weeks) as measured by loss upon ignition. These results are quite contrary to those observed by Wollny. As measured by production of carbon dioxide, the decomposition of wheat bran was greatest, followed by cottonseed meal, corn chops, manure, and cobs. Waksman (25) states that in the presence of large quantities of carbohydrates, molds compete with higher plants for available nitrogen compounds. Upon decomposition of the mold mycelium, the nitrogen is given back to the soil. Potter and Snyder (19) further showed that sterilized soils, with and without dextrose, inoculated with fungi decreased in nitrate nitrogen. Green manure decomposed much more rapidly than barnyard manure (18). In fifty-three days clover was 60.8 per cent decomposed, oats 49 per cent, and manure 42 per cent. Manure is naturally composed of decomposed organic residues which would decompose further only slowly. In work similar to some previously conducted by Wollny, Merkle (13) noted legumes decomposed more rapidly than straw and litters low in nitrogen. Sugar beets decomposed rapidly for a time. Swedes and rape gave nearly as much carbon dioxide as legumes. Forest litter gave less carbon dioxide than non-legumes and root crops. No very great differences in the rates of decomposition of these substances were noted contrary to many results of others.

The subject of nitrogen starvation of plants as a result of application of straw has received much attention. Kellerman (10) noted injury to citrus trees due to nitrogen starvation after fertilization with mature barley straw.

Rahn (20) studied the effects of the presence of available nitrogen on straw decomposition as measured by the loss of weight upon ignition and carbon dioxide produced. He found that nitrate or ammonium nitrogen accelerated the decomposition of the straw two days after its application to the soil; the nitrate appeared to be superior. The straw treated soils normally became deficient in nitrogen, but legumes did not cause this effect. As soon as the most of the organic matter has decomposed, there follows a slow and steady formation of ammonia and nitrate which is greater than the amounts originally present. There is apparently little or no loss of nitrogen by denitrification. After fifteen days, in the presence of nitrate, 15 per cent of the straw was decomposed. Manure, or straw composted with liquid manure containing more nitrogen than straw alone, did not cause nitrogen deficiencies in soils. Murray (15) studied the straw problem further and found that the excess energy material low in nitrogen greatly increased the numbers of bacteria temporarily, which organisms assimilated a proportionate amount of soluble nitrogen and other plant food elements. The straw did not, however, increase any one group of bacteria more than the others. He observed no loss in total nitrogen in the soil nor inhibition to the nitrification or ammonification processes. Scott (22) and Stephenson (23) noted similar effects from straw fertilization.

Lyon, Bizzell and Wilson (11) observed that roots of oats, timothy, and corn, upon decomposition, depleted the soil's store of nitrate far below that of the untreated soil. Clover had hardly any effect while dried blood increased the soil nitrates. These effects corresponded with the nitrogen contents of the materials. Gainey (6) noted effects similar to those from straw fertilization following treatment of the soil with paraffin oil.

Miyake and Nakamura (14) made use of the production of carbon dioxide in following the decomposition of soybean and herring cakes. They found that CaO stimulated decomposition more than did $CaCO_3$, but these sources of lime increased the soluble nitrogen in the reverse order, the amounts of organic nitrogen mineralized not being proportional to the amounts of organic matter decomposed. It is quite probable that the effects of lime on the decomposition of organic matter rich in nitrogen such as they used (7–11 per cent nitrogen) would be different from those on organic matters lower in nitrogen.

Waksman and Starkey (26) noted the decomposition of 43 per cent of alfalfa meal two weeks after its addition to soil. Potter and Snyder (17) recorded that increased amounts of carbon dioxide were produced from soils receiving increasing applications of manure. Lime further increased this carbon dioxide. Wollny (30) clearly demonstrated that carbon dioxide produced from soils to which different amounts of organic matter were added was not proportional to the amounts of these additions, due to the deficiency of oxygen and the sterilizing action of large amounts of carbon dioxide.

Influences of the nature of the organic matter upon the rapidity of its decomposition. Wollny (30) states that the intensity of the decomposition of organic matter largely depends upon the quantity and quality of the material added and its state of division. Organic matter which usually decomposes only with difficulty, as in the case of peat, can be made to decompose more easily if finely divided; in the case of easily decomposable material, such as pea vines, the fineness is relatively unimportant. Wollny and also Whiting and Schoonover (29) noted that plants in the green state decompose more readily than after drying and subsequent remoistening. These last named authors believed that curing hindered decomposition both by altering the chemical composition of the material and by destroying enzymes which facilitated decomposition of the green material by autolysis. The material was believed to become more horny and shriveled by drying. The leaves of plants decomposed more rapidly than their stems or roots; this was correlated with the higher nitrogen content of the leaves. This has also been shown more recently by Bal (3) and Martin (12) who found that younger and more succulent plants decomposed more rapidly. Dvořák (4) states that the fresh plant residues are most available largely since the lower carbohydrates are more abundant; in the older plants, the ligno-celluloses predominate.

Rates of decomposition. It has been repeatedly noticed that the decomposition of the more readily decomposable organic materials was greatest soon after their addition. The time

varied with the kind of organic matter used and the environmental conditions. Wollny states that organic matter decomposes with more difficulty as the alteration or decomposition is advanced. Van Suchtelen (24) mentions that, in general, the less abundant hexoses and pentosans decompose first followed by the polysaccharides, celluloses, pectins, starches, and albumins. A strongly resistant carbonaceous residue is left which, however, is decomposed slowly. Dextrose gave the maximum production of carbon dioxide the second day while green manure (oat straw) gave the maximum the sixth day (temperature used 10–12°C.). Fraps (5) found that oxidation was very rapid at the start and decreased after the first week. Potter and Snyder (18) found that clover decomposed rapidly while oats had a slow initial rate of decomposition. The carbon dioxide produced from inoculated sterile soils (19) was greatest the first few days whether additional organic matter was added or not. Gainey (7) obtained the maximum carbon dioxide the second day from dried blood and cottonseed meal, the former decomposing more rapidly. Hibbard (9), Rahn (20), Dvořák (4) and Waksman and Starkey (26) noted quite similar effects the first few days after the addition of organic matter to soils.

Decomposition by soils of different fertility. Wollny records that decomposition is more active in cultivated than in rarely cultivated soils. Fraps (5) states that the relative powers of soils to oxidize added organic matter are not very variable, but that the relative rates of production of carbon dioxide from the soils themselves show greater variation. Quite similar results have been repeatedly obtained in this laboratory

Correlations have been made between the decomposing powers of different soils and their fertility. This subject is somewhat completely discussed elsewhere (27).

Effects of organic matter on numbers of microörganisms. Since carbon dioxide is produced from the organic matter by microörganisms there occurs a simultaneous increase in the numbers of these organisms with the increase in carbon dioxide. Bacteria, fungi and actinomycetes all are prominent in organic matter decomposition, not all, however, being affected alike by different organic materials. This question has been recently considered in detail by Waksman and Starkey (28). Van Suchtelen concluded that production of carbon dioxide was a much more accurate index of the numbers and activities of these organisms than the numbers determined by the present plate and dilution methods. Russell (21) makes the following qualitative explanation of the effects of organic materials on microbiological activities:

	CHANGES IN NO₃ AND NH₃	NUMBERS OF MICROÖRGANISMS
Soil under normal conditions	Accumulation	Low and fluctuating
Soil plus carbohydrates	Decrease	Rapid increase then a decrease
Soil plus peptone	Increase	Rapid increase and rapid decrease

Injurious effects of some organic materials. Some of the organic matters added to, or occurring in soils have an injurious effect upon decomposition. Wollny states that the presence of resins, waxes, fats, and tannins, frequently occurring in peats are partly responsible for their slow decomposition. Dvořák believed that the terpenes and tannic acid in some organic materials had an unfavorable action on bacterial activity. Gibbs and Werkman (8) found sawdust, leaves, needles, cones and various tree products inhibited nitrification and ammonification and several years might pass before the detrimental materials disappeared.

METHODS

The soils used were put through a 3-mm. sieve after being brought to the laboratory. The alfalfa meal and rye straw were obtained a few weeks be-

fore starting the experiments, dried, and ground to pass through a $\frac{1}{2}$-mm. sieve. The cellulose was used in the form of finely cut filter paper. In general, one gram of the organic matter studied was incorporated with 100 gm. of soil. Distilled water was added in such amounts as to bring the soil to optimum moisture content. In some instances one gram of organic matter was used in 200 gm. of soil. Where dextrose was used, 500 mgm. were added in solution to 100 gm. of soil. The soils were kept in a constant temperature room at 25–28°C. as was also the apparatus used for determining the carbon dioxide produced from the soils. The apparatus used has been described in detail elsewhere (16, 27). Both the large and the small apparatus used in previous experiments has been used in these studies. Air free from carbon dioxide was constantly circulated over the surface of the soils at the rate of three liters per hour. Measurement of the carbon dioxide produced from these organic materials has given very satisfactory results In all cases the treatments were run in duplicate which determinations showed close agreements for work of this kind.

Total carbon determinations were made according to the official method of the Association of Agricultural Chemists (1). The nitrate determinations were made by the phenoldisulfonic acid method. Ammonia was determined by magnesium oxide distillation.

<center>RESULTS</center>

Decomposition of different organic materials in the same soil. In these experiments organic materials of widely different character have been used. Alfalfa meal and rye straw have been taken as examples of two types of organic matter commonly added to soils as green manures. Dried blood and cellulose have been used as examples of organic materials rich and poor in nitrogen, one of animal origin and readily decomposed, the other of plant origin and generally considered quite resistant to decomposition. The fungous material that has been used was obtained as mycelial and spore growth from cultural media, washed, dried and finally ground.[3] The question has frequently been raised as to the availability of the nitrogen which becomes stored in fungous and bacterial bodies. It seems that the carbon dioxide produced from such material should answer this question in part.

The amounts of nitrogen and carbon contained in the materials used are listed below:

	NITRO-GEN	CARBON		NITRO-GEN	CARBON
	per cent	*per cent*		*per cent*	*per cent*
Cellulose....................	0.00	44.44	Fungous material...........	3.84	44.31
Rye straw...................	0.72	36.40	Dried blood................	9.61	37.52
Alfalfa meal................	2.45	40.62	Dextrose...................	0.00	37.46

[3] The author is obliged to Mr. Heukelekian of this laboratory for the fungous material.

The air stream, after passing over the soils containing dried blood and fungous material, passed through standard sulfuric acid to remove the ammonia. All the organic materials except the cellulose were added to a fertile loam soil in amounts equivalent to one-half per cent of the weight of the soil. One per cent of cellulose was added. The data for this experiment are all calculated on the basis of 0.5 gm. of organic matter. Table 1 and figure 1 present the results. In this figure and those following, in place of plotting the actual amounts of carbon dioxide produced, the percentage of the carbon contained in the organic matter which was given off as carbon dioxide at the different intervals has been plotted. In all instances, the carbon dioxide from soils similarly treated but lacking the organic additions

TABLE 1

Rates (I) and Courses (II) of decomposition of some organic materials

ORGANIC MATTER USED	AFTER DIFFERENT PERIODS OF INCUBATION (DAYS)										TOTALS
	1	2	3	4	5	6	7	8	9	10	
I. Daily production of CO_2 in mgm.											
Cellulose.........	1.83	1.84	1.83	7.14	6.87	28.05	28.04	27.00	27.00	*33.46*	163.06
Rye straw........	*74.29*	29.31	37.83	22.98	16.65	12.59	13.08	12.93	9.77	9.77	239.20
Alfalfa meal......	*106.63*	67.83	68.24	37.42	27.79	15.48	14.58	13.76	8.33	8.32	368.38
Fungous material	*79.80*	44.44	63.70	62.46	57.92	41.34	33.44	27.80	16.58	16.58	444.06
Dried blood......	7.23	41.49	68.30	*82.33*	82.32	56.72	48.61	31.40	26.05	23.15	467.60
Dextrose.........	84.98	*156.52*									
II. Percentage decomposed at daily intervals											
Cellulose.........	0.23	0.45	0.68	1.55	2.39	5.84	9.28	12.59	15.90	*20.01*	
Rye straw........	*11.13*	15.52	21.19	24.64	27.13	29.02	30.98	32.91	34.38	35.84	
Alfalfa meal......	*15.98*	26.14	36.37	41.98	46.14	48.46	50.64	52.71	53.95	55.20	
Fungous material	*11.96*	18.62	28.16	38.20	46.20	52.40	57.41	61.57	64.06	66.54	
Dried blood......	1.05	7.08	17.01	*28.98*	40.95	49.19	56.26	60.83	64.61	67.98	
Dextrose.........	12.37	*35.16*									

has been substracted from the presented data. It is accordingly assumed that this carbon dioxide has all been produced from the organic matter added.

It is naturally apparent that in the same soil the amount of decomposition of different organic materials at any one time is different. The first few days show the greatest divergence in decomposition. At the two days' interval they vary from less than 0.5 per cent of the cellulose to over 35 per cent of the dextrose decomposed. This wide variation holds to a large extent throughout the period. After ten days, 20 per cent of the cellulose, 35 per cent of the rye straw and considerably over 50 per cent of the alfalfa meal, fungous material and dried blood have become decomposed. Unfortunately the dextrose determinations were discontinued after two days.

Decomposition of these organic materials in soil is extremely rapid. Although the conditions used approach the optimum and are far more favor-

able than those in the field, it is only reasonable to consider that such organic materials would largely disappear even under normal field conditions in a very short time.   The periods of maximum decomposition are indicated in the table by italics.   It is noted that, in general, the period of maximum decomposition occurs the first day after addition of these materials to the
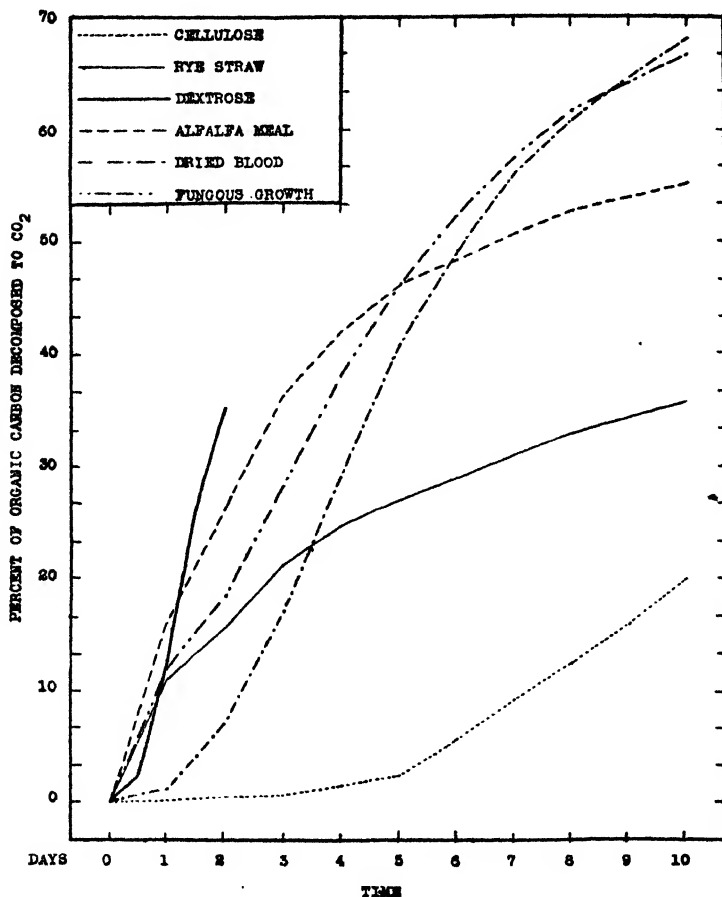
FIG. 1. COURSES OF DECOMPOSITION OF SOME ORGANIC MATERIALS IN SOIL

soil.   This is the case with the rye straw, alfalfa meal, and fungous material. Dextrose shows the maximum decomposition the second day.   Although this material was not studied further here, numerous experiments have indicated the assumption to be correct that dextrose decomposes most rapidly the first 48 hours in fertile soil.   In the case of cellulose the decomposition

is most rapid on the tenth day. The dried blood gave maximum daily decomposition the fourth day.

The rate of decomposition with each organic material is distinctive. Cellulose exhibits a very marked and extended lag before the decomposition becomes at all rapid. Dried blood also exhibits this lag although for a much shorter time. It is suggested that this lag may be accounted for by a lack of any abundance of the organisms which attack these materials at the time of their addition to the soil. As the organisms become more numerous, the decomposition proceeds more rapidly, very much more so with the dried blood. Alfalfa meal, rye straw, and the fungous material show a rapid initial decomposition. Dextrose decomposes much slower the first few hours than during the period immediately following.

Cellulose decomposes more slowly than rye straw and both decompose more slowly than the other substances used. If the first few days alone are considered, alfalfa meal, dried blood, and fungous material do not vary greatly from one another. However, if completeness of decomposition is considered over a longer period, dried blood and the fungous material decompose appreciably further than the alfalfa. Although dextrose was not considered sufficiently, this would undoubtedly have exceeded all of the others. The fungous material is evidently very rapidly decomposed even more so than dried blood. Apparently, when dead, fungous material would quickly disappear in soil.

Wollny's frequently quoted statement that animal products disappear more rapidly in soils than plant products should not be accepted without any qualifications. Certainly some plant products such as the lower carbohydrates and also the fungous mycelium used in these experiments exhibit extremely rapid decomposition. It is important to note that, with the exception of dextrose, the slowest decomposing substances, namely cellulose and rye straw are poorest in nitrogen. Dextrose, however, decomposes very rapidly because it is attacked by the nitrogen-fixing bacteria in the soil, capable of obtaining their nitrogen from the atmosphere. These organisms are unable, however, to utilize celluloses as such and, therefore, the available nitrogen becomes a controlling factor. Even where sufficient nitrogen is present during the decomposition of rye straw and cellulose, the process is not nearly as rapid as with the other materials used as will be shown later. Further, alfalfa does not create nitrogen deficiency yet it decomposes much less completely than dried blood or fungous material in the period used. There are undoubtedly limitations to decomposition other than nitrogen deficiency.

Nitrogen exchanges in the presence of decomposing organic matter. The effects of nitrates on the decomposition of rye straw and alfalfa meal have been studied. One-gram portions of rye straw and alfalfa meal were added to 200-gm. portions of soil with and without 0.05 gm. $NaNO_3$. The results are given in table 2 and figure 2. Nitrate has not increased the decomposi-

tion of alfalfa meal, in fact the soil to which nitrate has been added gave less carbon dioxide than the one lacking it. The differences between the two are not believed to have been caused by the nitrate. Nitrate distinctly favored straw decomposition. This effect of the nitrate was noticed on the third day and continued to increase decomposition over the straw lacking the nitrate to the end of the period.

The nitrogen exchanges in the presence of rye straw, alfalfa meal, and dried blood may throw light upon the decomposition of these organic materials. In table 3 are listed the nitrate and ammonia determinations from soils treated with these organic materials with and without nitrate. As would be expected, the ammonium and nitrate nitrogen increased in the untreated soil.

TABLE 2

Decomposition of rye straw and alfalfa meal with and without added nitrates

| TREATMENT | PERIOD OF INCUBATION (DAYS) | | | | | | | | | | TOTALS |
	1	2	3	4	5	6	7	8	9	10	
Daily production of CO_2 in mgm.											
Rye straw[1]......	48.33	52.96	42.55	34.14	29.23	27.20	22.57	24.02	19.68	22.57	323.25
Rye straw + NaNO₃.........	43.12	53.83	69.16	68.29	57.88	55.85	46.88	47.46	37.91	39.06	519.44
Alfalfa meal......	170.84	174.51	109.40	70.32	50.06	41.67	30.96	29.81	22.57	24.31	724.45
Alfalfa meal + NaNO₃.........	180.29	156.56	102.73	63.95	44.85	38.49	27.78	25.18	19.68	21.12	680.63
Percentage decomposition at daily intervals											
Rye straw........	3.13	6.55	9.30	11.51	13.40	15.16	16.62	18.17	19.45	20.91	
Rye straw + NaNO₃.........	2.79	6.27	10.74	15.16	18.90	22.52	25.55	28.62	31.07	33.59	
Alfalfa meal......	11.71	23.66	31.16	35.98	39.41	42.27	44.39	46.43	47.98	49.85	
Alfalfa meal + NaNO₃.........	13.36	23.08	30.12	34.50	37.58	40.21	42.12	43.84	45.19	46.64	

[1] Rye straw = 42.17 per cent C.

In the presence of rye straw the nitrate nitrogen entirely disappeared and the ammonium nitrogen did not change appreciably from the control. At the end of the incubation period this soil had a deficiency in soluble nitrogen over that in the control. Where the nitrate was added with the straw the ammonium nitrogen remained unchanged, but the nitrate increased almost reaching that in the control. With the alfalfa meal alone the ammonia did not change but the nitrates increased showing a marked increase in soluble nitrate over the control. There was also an increase in nitrate nitrogen where nitrate was added with the alfalfa, this being twice as great as in the absence of added nitrate. Where the dried blood was added, both the ammonium and nitrate nitrogen increased, the first more than seven times as much as

the second, resulting in a remarkably high increase in soluble nitrogen. It is observed that ammonia was brought over in the air current only from the soils treated with dried blood, in which case the decomposition liberated more ammonia than the soil could hold.
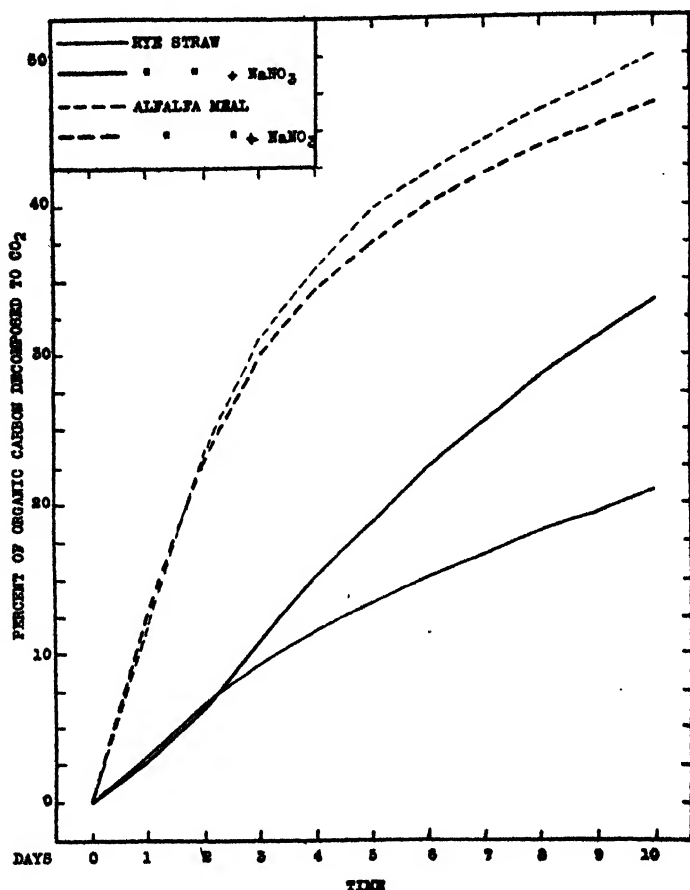
FIG. 2. EFFECTS OF NITRATE ON THE COURSES OF DECOMPOSITION OF RYE STRAW AND ALFALFA MEAL

Apparently there was no nitrogen deficiency except where straw was used without additional nitrate. The amounts of organic matter decomposed, as determined by the carbon dioxide produced should free a definite amount of nitrogen to be either reassimilated or given off as a waste product in the form of ammonia which becomes oxidized more slowly to nitrate. The last

column in table 3 gives this calculated amount of nitrogen. In the case of rye straw and the alfalfa without nitrate there is a considerable deficiency in soluble nitrogen accumulated as compared with the amount probably liberated. However, where nitrate was added with the alfalfa meal and with dried blood there is an excess accumulation over that assumed to be liberated.

TABLE 3

Ammonium and nitrate nitrogen transformations in soils treated with some organic materials

SOIL TREATMENT	NITROGEN CONTENT AT START			NITROGEN CONTENT AT END					INCREASE OR DECREASE IN SOLUBLE N	INCREASE OR DECREASE IN N OVER CONTROL	N ADDED IN ORGANIC MATTER	CALCULATED N IN ORGANIC MATTER DECOMPOSED
	NH_4-N	NO_3-N	Total soluble N	NH_4-N in soil	NH_4-N in air stream	Total NH_4-N	NO_3-N	Total soluble N				
	mgm.	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*
Untreated....	1.74	0.16		2.04	0.36		2.13					
Untreated....				2.60	0.07		5.11					
Average.....	*1.74*	*0.16*	*1.90*	*2.32*	*0.22*	*2.54*	*3.62*	*6.16*	*4.26*			
Rye straw....	1.62	0.12		3.16	0.07		0.00				7.14	
Rye straw....				2.04	0.22		0.00				7.22	
Average.....	*1.62*	*0.12*	*1.74*	*2.60*	*0.15*	*2.75*	*0.00*	*2.75*	*1.01*	*−3.25*	*7.18*	*1.78*
Rye straw + NO_3........	1.74	3.09		1.44	0.36		6.71					
Rye straw + NO_3........				1.44	0.45		7.24					
Average.....	*1.74*	*3.09*	*4.83*	*1.44*	*0.40*	*1.84*	*6.98*	*8.82*	*3.99*	*−0.27*	*7.18*	*2.94*
Alfalfa meal..	2.46	0.20		2.04	0.36		11.71				24.75	
Alfalfa meal..				2.60	0.00		9.94				24.25	
Average.....	*2.46*	*0.20*	*2.66*	*2.32*	*0.18*	*2.50*	*10.83*	*13.33*	*10.67*	*6.41*	*24.50*	*13.36*
Alfalfa meal + NO_3......	1.74	4.39		2.04	0.00		23.95					
Alfalfa meal + NO_3......				2.60	0.00		20.76					
Average.....	*1.74*	*4.39*	*6.13*	*2.32*	*0.00*	*2.32*	*22.36*	*24.68*	*18.55*	*14.29*	*24.50*	*12.46*
Dried blood...	1.62	3.19		58.00	7.00		16.93				86.45	
Dried blood...				75.92	14.94		10.64				105.79	
Average.....	*1.62*	*3.19*	*4.81*	*66.96*	*10.97*	*77.93*	*13.79*	*91.72*	*86.91*	*82.65*	*96.12*	*73.00*

The organic materials added were composed of many compounds and apparently either the parts higher in nitrogen were decomposed in these instances or else the organic matter decomposed considerably further than the carbon dioxide produced indicated, both of which would tend to explain these differences.

It may be concluded from these results on the early stages of organic matter decomposition (1) that rye straw tends to deplete soluble soil nitrogen, (2) that alfalfa does not greatly affect the supply of soluble soil nitrogen, not drawing on this supply but slightly adding to it, and (3) that dried blood immediately increases the soil's supply of soluble nitrogen considerably, the ammonia in particular, which more slowly becomes oxidized. These effects closely correlate with the percentages of nitrogen in the organic materials (see pages 10 and 11).

Decomposition in soils of different fertility. The soils used were from the experimental plots and varied greatly in fertility:

SOIL NUMBER	TREATMENT	FERTILITY
5A	Manure	Very fertile
5B	Manure plus lime	Very fertile
7A	Untreated	Extremely poor
7B	Lime	Fair
9A	$NaNO_3$ plus K and P minerals	Good
11B	$(NH_4)_2SO_4$ plus K and P minerals plus lime	Good

In these studies 1-gram portions of organic matter in the forms of cellulose, rye straw and dried blood were added to 100-gm. portions of soil. Additions of 0.10 gm. $NaNO_3$ were made to some of the soils containing cellulose. The incubation period used for cellulose was longer than usual since in a short time there was very little decomposition. As previously, in the case of the dried blood, the air stream passed through standard sulfuric acid after being drawn over the soil in order to trap the ammonia given off. Dextrose has been used in similar experiments reported elsewhere (27) and this organic matter is given consideration at this point. The results are found in tables 4–6 and figures 3–5.

The most evident fact is that decomposition of the same material is different in different soils. However, the order of the rapidity with which the different soils decompose one organic matter is not the same for a different organic material. It has previously been reported concerning decomposition of dextrose and alfalfa (27) that they effect greater evolution of carbon dioxide from soils that had received lime treatment than from similar soils not treated with lime. In general, the carbon dioxide produced was also correlated with the amounts of crops produced from these soils. The production of carbon dioxide from dextrose in soils varies during the first few days more than from most of the other organic materials studied.

The decomposition of cellulose, rye straw and dried blood shows somewhat similar relationships although this is not at all consistent. Cellulose in particular shows this. Further, the acceleration of decomposition of cellulose caused by nitrate is also very apparent here as shown previously with rye straw. Even under particularly favorable conditions in the fertile soil 5A,

TABLE 4

Decomposition of cellulose in soils of different fertility

Daily production of CO_2 in mgm.

TREATMENT	PERIOD OF INCUBATION (DAYS)																	TOTALS
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	
Soil 5A	4.37	4.37	4.37	12.90	12.37	18.14	18.14	17.14	17.14	14.84	14.84	14.84	10.54	11.73	11.73	11.73	11.73	209.73
Soil 5A + NaNO₃	3.67	3.67	3.67	14.27	13.74	56.09	56.09	53.99	53.99	66.91	66.91	66.91	41.06	32.63	32.63	32.63	32.63	639.92
Soil 7A	1.25	1.25	1.25	0.33	0.33	2.88	2.88	2.54	2.54	4.27	4.27	4.27	4.46	4.46	4.46	4.46	4.46	50.36
Soil 7A + NaNO₃	0.15	0.15	0.15	0.61	0.61	7.27	7.27	6.93	6.93	13.26	13.26	13.26	13.26	17.48	17.48	17.48	17.48	148.81
Soil 7B	3.91	3.91	3.91	3.91	5.36	5.09	5.09	7.27	7.27	5.25	5.25	5.25	4.63	4.63	4.63	4.63	4.63	84.62
Soil 7B + NaNO₃	2.44	2.44	2.44	6.11	7.56	20.49	20.49	33.95	33.95	30.55	30.55	30.55	33.12	27.99	27.99	27.99	27.99	371.73

Percentage decomposed at daily intervals

TREATMENT	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Soil 5A	0.27	0.54	0.80	1.60	2.36	3.47	4.58	5.63	6.69	7.60	8.51	9.42	10.06	10.71	11.43	12.15	12.87
Soil 5A + NaNO₃	0.23	0.45	0.68	1.55	2.39	5.84	9.28	12.59	15.90	20.01	24.06	28.22	30.74	33.26	35.26	37.27	39.27
Soil 7A	0.08	0.15	0.23	0.25	0.27	0.45	0.62	0.78	0.94	1.20	1.46	1.72	2.00	2.27	2.54	2.82	3.09
Soil 7A + NaNO₃	0.01	0.02	0.03	0.07	0.10	0.55	0.99	1.42	1.85	2.66	3.47	4.29	5.10	5.91	6.99	8.06	9.13
Soil 7B	0.24	0.48	0.72	0.96	1.29	1.60	1.91	2.36	2.81	3.13	3.45	3.77	4.06	4.34	4.62	4.91	5.19
Soil 7B + NaNO₃	0.15	0.30	0.45	0.82	1.29	2.55	3.80	5.89	7.97	9.84	11.72	13.28	15.63	17.66	19.38	21.09	22.81

TABLE 5

Decomposition of rye straw in soils of different fertility

SOIL	PERIOD OF INCUBATION (DAYS)										TOTALS
	1	2	3	4	5	6	7	8	9	10	

Daily production of CO_2 in mgm.

5A	*51.10*	45.08	20.13	20.12	14.86	14.86	14.86	11.59	11.59	11.58	215.77
5B	*56.00*	27.59	14.88	14.88	14.06	14.06	14.06	11.56	11.56	11.56	190.21
7A	*35.64*	19.93	12.46	12.46	10.10	10.10	10.10	6.74	6.74	6.74	131.01
7B	*49.88*	26.18	16.75	16.75	16.27	16.27	16.27	10.36	10.36	10.36	189.45
9A	32.34	*45.97*	19.11	19.11	16.97	16.97	16.97	9.01	9.01	9.01	194.47
11B	*53.31*	28.17	18.73	18.73	15.59	15.59	15.59	10.16	10.16	10.16	196.19

Percentage decomposed at daily intervals

5A	*3.83*	7.21	8.72	10.22	11.34	12.45	13.56	14.43	15.30	16.17	
5B	*4.20*	6.27	7.38	8.49	9.55	10.60	11.65	12.52	13.39	14.25	
7A	*2.67*	4.16	5.10	6.03	6.79	7.54	8.30	8.81	9.31	9.82	
7B	*3.74*	5.70	6.95	8.21	9.43	10.65	11.87	12.64	13.42	14.20	
9A	2.42	*5.87*	7.30	8.73	10.00	11.27	12.54	13.22	13.90	14.57	
11B	*3.99*	6.11	7.49	8.91	10.08	11.25	12.42	13.18	13.94	14.70	

TABLE 6

Decomposition of dried blood in soils of different fertility

SOIL	PERIOD OF INCUBATION (DAYS)										TOTALS
	1	2	3	4	5	6	7	8	9	10	

Daily production of CO_2 in mgm.

5A	19.00	73.35	104.00	97.97	90.63	*112.26*	90.43	103.44	69.06	65.30	825.44
5B	29.60	133.86	*165.81*	152.97	110.55	121.74	96.79	77.14	79.74	61.55	1029.75
7A	10.74	37.20	53.97	77.02	91.15	134.07	130.02	*143.31*	102.28	82.93	862.69
7B	29.08	71.52	91.95	111.34	98.23	*126.33*	88.55	83.21	79.17	60.39	839.77
9A	13.23	45.46	67.85	74.13	71.77	102.27	101.12	*103.15*	103.15	82.64	764.77
11B	35.24	86.05	110.94	*116.04*	94.92	112.52	79.45	73.68	58.08	41.61	808.53

Percentage decomposed at daily intervals

5A	1.06	6.07	13.31	20.11	26.33	*34.13*	40.35	47.57	52.30	56.75	
5B	1.87	11.32	*23.10*	33.93	41.67	50.22	56.96	62.32	67.86	72.08	
7A	0.72	3.37	7.24	12.78	19.32	28.31	38.33	*48.63*	55.95	61.86	
7B	1.80	6.68	13.05	20.83	27.76	*36.73*	42.96	48.77	54.30	58.46	
9A	0.86	4.06	8.88	14.16	19.27	26.59	33.79	*41.20*	48.58	54.46	
11B	2.32	8.34	16.17	*24.36*	31.07	39.05	44.63	49.80	53.84	56.69	

further improved by the addition of $NaNO_3$, the cellulose was only about 40 per cent decomposed in seventeen days as compared with dextrose which was more than 35 per cent decomposed in two days. The extremely slow initial decomposition of cellulose is strikingly apparent.

There are no very wide differences between the different soils with respect to their abilities to decompose rye straw. The production of carbon dioxide is generally uniformly low. In general, the richer soils tend to decompose rye straw more rapidly than the poorer soils. There were undoubtedly deficiencies in soluble nitrogen in all of these soils early in the stage of decomposition which limited the process later.
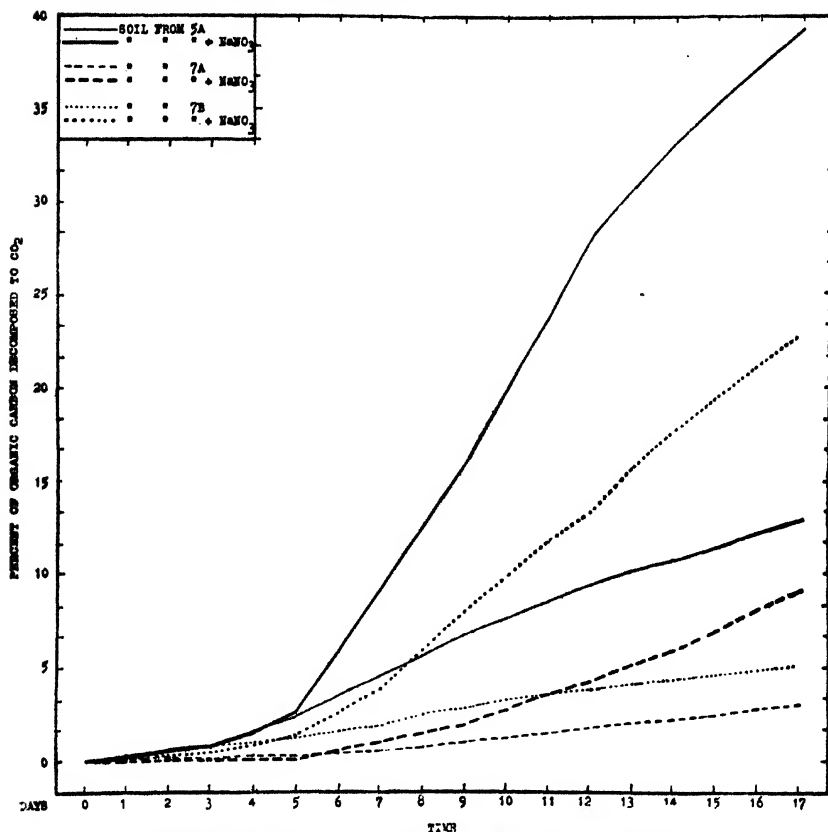
FIG. 3. EFFECTS OF NITRATE ON THE COURSES OF DECOMPOSITION OF CELLULOSE IN SOILS OF DIFFERENT FERTILITY

Decomposition of dried blood was very rapid in all of the soils following the characteristic initial lag. However, there is no consistent correlation here between the amount decomposed in the soils and their fertility. This is principally caused by the abundant ammonia production which tended to bring all of the soils to an alkaline condition. In the more nearly neutral

poorly buffered soils the reaction evidently became too alkaline for favorable decomposition.

The changes in soluble nitrogen in these soils are presented in table 7. The nitrate changes have been negligible, but the increases in ammonium nitrogen are considerable and account for practically all of the increase in
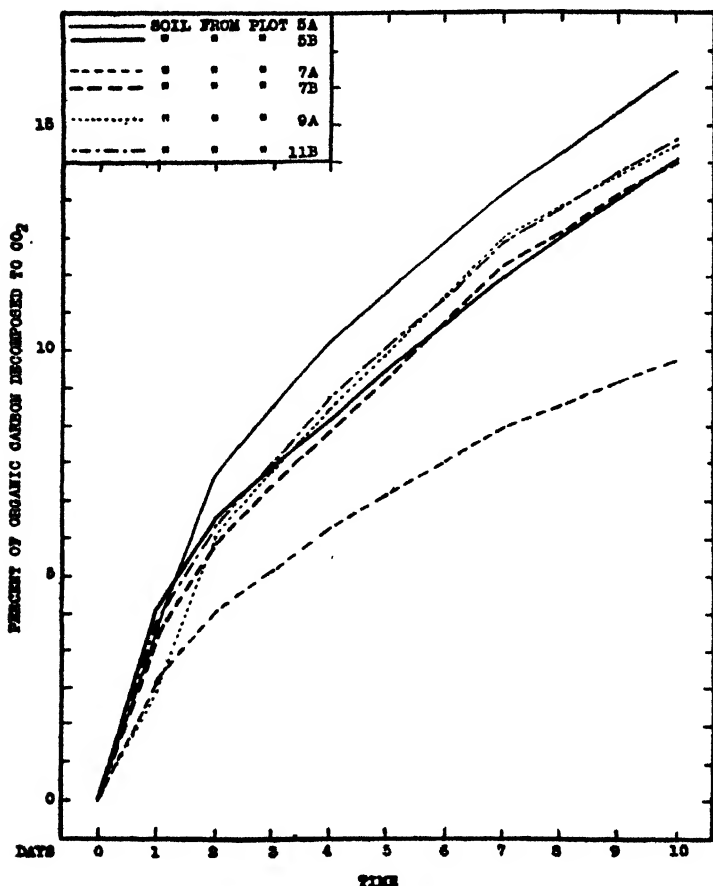
FIG. 4. COURSES OF DECOMPOSITION OF RYE STRAW IN SOILS OF DIFFERENT FERTILITY

soluble nitrogen in the soil, amounting to 35–70 mgm. in the different soils. A large part of the ammonia produced in the more nearly neutral soils was trapped from the air stream, while less was drawn from the more acid soils, more being retained in the soils themselves. A comparison between the determined increase in soluble nitrogen with that calculated to have been

liberated from the amounts of dried blood decomposed bring out some differences. It is noted that from the more acid soils (5A, pH 5.5; 7A, pH 5.1; 9A, pH 5.8 and 11B, pH 6.0) the soluble nitrogen recovered is distinctly less than that assumed to be liberated. In soils 5B (pH 6.7) and 7B (pH 6.5)
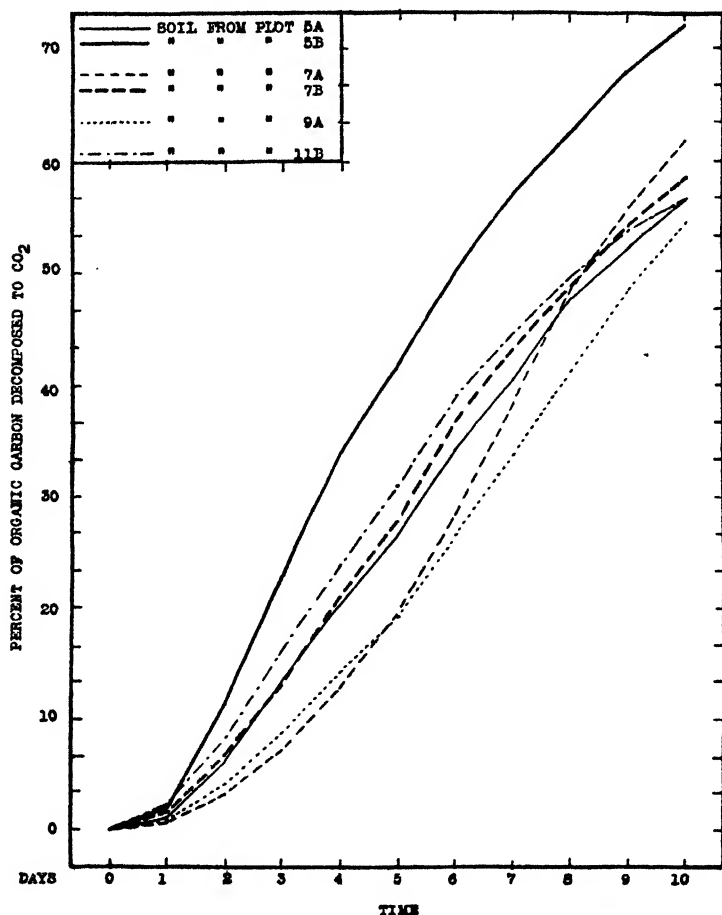
FIG. 5. COURSES OF DECOMPOSITION OF DRIED BLOOD IN SOILS OF DIFFERENT FERTILITY

there are scarcely any differences between the amounts of soluble nitrogen recovered and those calculated to have been liberated. This can be explained by a proper understanding of the organisms affecting the decomposition in the different instances. Although bacteria were very active in all cases, the fungi made particularly abundant development in the more acid soils and the

actinomycetes also developed in the soils later due to the favorable alkaline reaction created by the ammonia. In the more nearly neutral soils the fungi made a comparatively scant development and the decomposition was effected almost entirely by the bacteria. The deficiencies in soluble nitrogen in the acid soils are accounted for in the amounts assimilated by the fungi, since these organisms are much more economical than the bacteria in the decomposition of organic matter assimilating much larger portions of carbon and nitrogen per unit of organic matter decomposed.

TABLE 7

Ammonium and nitrate nitrogen transformations in soils treated with dried blood

SOIL NUMBER	NITROGEN CONTENT AT START			NITROGEN CONTENT AT END					INCREASE IN SOLUBLE N	N ADDED IN ORGANIC MATTER	CALCULATED N IN AMOUNT ORGANIC MATTER DECOMPOSED
	NH_3-N	NO_3-N	Total soluble N	NH_3-N in soil	NH_3-N in air stream	Total NH_3-N	NO_3-N	Total soluble N			
	mgm.	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*
5A	2.24	3.68		32.39	2.93		6.91				
5A				34.88	4.11		5.99				
Average..	*2.24*	*3.68*	*5.92*	*33.64*	*3.52*	*37.16*	*6.45*	*43.61*	*37.69*	*96.12*	*54.55*
5B	1.79	3.78		20.07	54.86		2.25				
5B				19.77	50.17		2.81				
Average..	*1.79*	*3.78*	*5.57*	*19.92*	*52.52*	*72.44*	*2.53*	*74.97*	*69.40*	*96.12*	*69.28*
7A	1.49	3.27		33.56	14.37		2.50				
7A				34.00	13.20	·	2.05				
Average..	*1.49*	*3.27*	*4.76*	*33.78*	*13.79*	*47.57*	*2.28*	*49.85*	*45.09*	*96.12*	*59.46*
7B	1.64	3.59		20.87	35.20		2.75				
7B				21.39	36.08		2.66				
Average..	*1.64*	*3.59*	*5.23*	*21.13*	*35.64*	*56.77*	*2.71*	*59.48*	*54.25*	*96.12*	*56.19*
9A	2.09	0.99		32.31	4.25		3.99				
9A				32.24	3.08		3.99				
Average..	*2.09*	*0.99*	*3.08*	*32.28*	*3.67*	*35.95*	*3.99*	*39.94*	*36.86*	*96.12*	*52.35*
11B	1.79	3.17		19.48	11.44		6.65				
11B				19.04	15.84		5.99				
Average..	*1.79*	*3.17*	*4.96*	*19.26*	*13.64*	*32.90*	*6.32*	*39.22*	*34.26*	*96.12*	*54.49*

Figures 3–5 exhibit largely the same characteristics in the different soils as those shown previously for the decomposition in one soil. The differences appear to be largely quantitative and not qualitative.

From these and other results (27) the further conclusion seems justified that the differences in the carbon dioxide produced from the carbon in the soils without other additions of organic matter are much greater than the differences in carbon dioxide produced by these same soils from added organic matter.

DISCUSSION

Contrary to the opinions expressed by Whiting and Schoonover that production of carbon dioxide was not as good an index of the decomposition as nitrate-nitrogen accumulation, the author has found the measurement of carbon dioxide very satisfactory. The fact as stated that there is no true relation between the carbon oxidized and the nitrogen nitrified speaks rather against the measurement of nitrate nitrogen. Their results on the amounts of clover decomposed for different periods as indicated by nitrate accumulation are decidedly lower than those obtained by many other workers using production of carbon dioxide. It is further apparent from the results recorded in this paper and particularly those recently presented by Lyon, Bizzell and Wilson (11) that the accumulation of soluble nitrogen is not proportional to the decomposition of clover and alfalfa. This is largely due to the fact that the nitrogen becomes practically all temporarily assimilated into the microbial bodies during the decomposition of materials containing about 2 per cent nitrogen. Further, the kinds of organisms active in the decomposition as regulated by the soil conditions will greatly affect the amount of nitrogen liberated and reassimilated. Besides the greater accuracy of the method for determining organic matter decomposition. the rate of the decomposition may more easily be followed by measuring carbon dioxide evolved than by determining nitrate accumulation.

The rapidity of decomposition of some crude organic materials such as rye and alfalfa may be associated somewhat with their nitrogenous composition. However, nitrogen is far from being the only limiting factor. Some organic materials decompose easily and others with much more difficulty irrespective of their nitrogenous contents. As an example, dextrose and cellulose may be cited. These two compounds both entirely lack nitrogen. One, the dextrose, decomposed the most readily of all the materials studied, even those very rich in nitrogen; the other, cellulose, decomposed the slowest of all those considered. Apparently no broad generalizations apply to the relative ease of decomposition on the basis of carbon, nitrogen nor oxygen contents. It is probably true, however, that the simpler organic materials, due to the readiness with which they are attacked by all lower organisms do decompose most readily, while the more complex ones, by reason of the few organisms that can attack them are decomposed more slowly.

SUMMARY

The decomposition of cellulose, dextrose, rye straw, alfalfa meal, dried blood, and mixed spore and mycelium material of fungi has been followed in the same soil and, in some cases, in soils of different fertility by determining the carbon dioxide evolved. The results lead to the following conclusions:

1. The carbon dioxide evolved from decomposing organic matter serves as a reliable index of the process of decomposition.

2. In the same soil, the amount of decomposition of different organic materials at any one time is different.

3. Decomposition of the organic materials is very rapid in fertile soils. After two days, 35 per cent of the carbon in dextrose had been given off as carbon dioxide, 26 per cent of the alfalfa meal, 19 per cent of the fungous material, 16 per cent of the rye straw, 7 per cent of the dried blood, and 0.5 per cent of the cellulose. The decomposition after ten days was 68 per cent of the dried blood, 67 per cent of the fungous material, 55 per cent of the alfalfa meal, 36 per cent of the rye straw, and 20 per cent of the cellulose. It is noteworthy that fungous material decomposes very rapidly.

4. During the first few days the differences in decomposition of the different materials are greatest.

5. In general, the period of maximum decomposition was one of the first few days after adding the material to the soil.

6. The rate with which each organic material decomposes is distinctive, some decomposing rapidly from the start, others showing a decided lag in the early stages of decomposition, and still others showing a uniformly moderate decomposition.

7. Cellulose decomposes most slowly, followed by the rye straw, in turn followed by alfalfa meal, fungous material and dried blood. Dextrose decomposes the most rapidly of all the materials used.

8. Nitrate distinctly accelerated decomposition of rye straw and cellulose but was inaffective when added to alfalfa meal. The effect of the nitrate on straw decomposition was noted on the third day. It continued to hasten decomposition to the end of the period.

9. Rye straw tends to deplete the soluble nitrogen in the soil during the early stages of decomposition; alfalfa meal slightly increases it; and dried blood greatly increases it, particularly the ammonia. These effects are correlated with the nitrogen contents of the organic materials.

10. The decomposition of the same material in soils of different fertility is different, but the order of the soils with respect to the rapidity with which they decompose one organic material is not the same for another. In general, however, fertile soils decompose organic matter more rapidly than those less productive and soils nearly neutral decompose organic matter more rapidly than those more acid.

11. The differences in production of carbon dioxide from the carbon contained in soils without further additions of organic matter are much greater than the differences in carbon dioxide produced from these same soils from added organic matter. The decomposing powers of different soils for most organic materials do not vary greatly.

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SORGHUM AS AN INDICATOR OF AVAILABLE SOIL-NITROGEN

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In an earlier paper (1) the writer has described greenhouse experiments showing that the hydrocyanic acid content of sorghum plants increases with the amount of nitrate applied, and has suggested the use of sorghum as an indicator plant in studies on the readily available nitrogen in soils. The present paper reports a trial of this suggestion under field conditions. The method used for the determination of the hydrocyanic acid has been the same as that described in the earlier paper.

PLOTS ON UNIVERSITY FARM

On June 12, 1923, sorghum was sown thickly in drills six inches apart, in two fields on the Minnesota Experiment Station Farm. Both fields had a fertile soil. Site I had been in a rotation including legumes, while site II had been continuously in legumes for several years. Six days later, when the plants were well up, plots one rod square were marked off, and sodium nitrate was scattered over them, at the rates of 0, 200, 400, 800, and 1600 pounds per acre.

Five days after the nitrate had been applied, two inches of rain fell (table 1), and there was some flooding, and probably some of the nitrate was washed away. In the case of site II, additional plots were marked off and nitrate applied on June 29 as before, taking care to use for these only portions of the field that were too high to have received any run-off from the previously fertilized plots.

Table 1 shows the rainfall during the time of the experiment.

Samples were taken and the prussic acid determined, first on June 29, next on August 6, and lastly on September 4 (tables 2, 3, and 4).

On June 29 all the plots that had received nitrate presented a spotted appearance, showing some stunted and some dead plants, the number of the latter increasing with the amount of nitrate applied. These spots were no doubt due to excessive amounts of nitrate, as the application by hand could not be made entirely uniform, thus producing an "alkali" effect upon the young plants, stunting them for a time, or killing them outright where the nitrate solution became too strong. The prussic acid content on June 29 is given in table 2. The transitory stunting effect of the nitrate is best shown in the weight of plants from site II, the plants on all the fertilized plots at that site being smaller than on the unfertilized plot.

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At the second sampling (table 3) the height of the plants with the leaves stretched upward was measured, and the weight of the green plants per square meter was determined, cutting them as low as possible. In the plants from plot 2, site I, the percentage of dry matter also was determined, and found to be 13.35 per cent.

TABLE 1

Rainfall at University Farm from June 1, to September 3, 1923

JUNE		JUNE		JULY		AUGUST	
Date	Amount	Date	Amount	Date	Amount	Date	Amount
	inches		*inches*		*inches*		*inches*
4	0.20	20	0.05	5	0.11	2	0.13
5	0.02	23	0.22	10	0.45	8	0.17
7	0.56	24	0.17	11	0.16	11	0.21
13	0.45	25	2.00	27	0.87	21	1.31
18	0.56	26	0.07	29	0.35	28	0.08
19	0.60	28	0.05	30	0.96		
Totals...............		4.95		2.90		1.90	
Total for the period.....						9.75	

TABLE 2

Hydrocyanic acid found on June 29 in sorghum plants 17 days after seeding

PLOT	NITRATE APPLIED		AVERAGE HEIGHT OF PLANTS	AVERAGE WEIGHT OF PLANTS	HYDROCYANIC ACID (HCN) FOUND PER PLANT	
	Per plot	Per acre				
	lbs.	*lbs.*	*cm.*	*gm.*	*per cent*	*mgm.*
Plots on Site I						
1	None	None	11	0.155	0.30	0.465
2	1.25	200	14	0.232	0.27	0.628
3	2.50	400	14	0.188	0.28	0.528
4	5.00	800	14	0.185	0.50	0.926
5	10.00	1600	14	0.200	0.42	0.840
Plots on Site II						
6	None	None	18	0.490	0.30	1.470
7	1.25	200	15	0.322	0.50	1.610
8	2.50	400	14	0.262	0.53	1.390
9	5.00	800	13	0.233	0.39	0.910
10	10.00	1600	15	0.200	0.54	1.080

The data show that on university farm soil, which is well supplied with available nitrogen, the addition of sodium nitrate increased the yield of green sorghum from 15 to 80 per cent, and the hydrocyanic acid in the green material still more. Since the first analysis, thirty-eight days before, the hydrocyanic acid *per plant* on the unfertilized plots had diminished by about one half,

while it had *increased* on six of the eight fertilized plots, and in general had increased more on the heavily fertilized than on the lightly fertilized ones.

TABLE 3

Relative growth and hydrocyanic acid found in sorghum plants on August 6, 35 days after seeding

PLOT NUMBER	NITRATE APPLIED PER ACRE	AVERAGE HEIGHT OF PLANTS	WEIGHT OF GREEN SORGHUM PER SQUARE METER	AVERAGE WEIGHT OF PLANTS	HYDROCYANIC ACID (HCN) FOUND			
					In leaves	In stems	In whole plant	Per whole plant
	lbs.	cm.	gm.	gm.	per cent	per cent	per cent	mgm.
Plots on Site I								
1	None	91	2160	6	0.0069	0.0016	0.0035	0.210
2	200	122	3200	19	0.0076	0.0038	0.0045	0.856
3	400	122	3420	25	0.0150	0.0014	0.0079	1.975
4	800	113	3035	25	0.0120	0.0034	0.0063	1.575
5	1600	113	3905	26	0.0130	0.0051	0.0077	2.002
Plots on Site II								
6	None	152	2990	18	0.0083	0.0017·	0.0040	0.720
7	200	165	3520	20	0.0078	0.0021	0.0040	0.800
8	400	167	3580	17	0.0115	0.0035	0.0065	1.105
9	800	172	3740	42	0.0177	0.0029	0.0078	3.280
10	1600	178	3470	25	0.0174	0.0024	0.0078	1.950

TABLE 4

Hydrocyanic acid found on September 4 in sorghum plants 88 days after seeding

PLOT	NITRATE APPLIED PER ACRE	AVERAGE WEIGHT OF PLANTS	HYDROCYANIC ACID (HCN) FOUND			
			In leaves	In stems	In whole plant	Per whole plant
	lbs.	gm.	per cent	per cent	per cent	mgm.
Site I						
1	None	29	Trace	Trace	Trace	Trace
2	200	37	0.00018	0.00006	0.00009	0.033
3	400	30	0.00030	0.00026	0.00027	0.083
4	800	28	0.00550	0.00260	0.00330	0.924
5	1600	27	0.00490	0.00260	0.00320	0.864
Site II						
6	None	26	0.00550	0.00140	0.00180	0.468
7	200	36	0.00850	0.00070	0.00310	1.116
8	400	32	0.00620	0.00120	0.00250	0.800
9	800	58	0.00460	0.00120	0.00190	1.102
10	1600	46	0.00720	0.00130	0.00340	1.564

It should be pointed out, however, that on two of the fertilized plots the weight of hydrocyanic acid per plant had diminished, and that there is no

distinct parallel between the amount of nitrate added and the amount of hydrocyanic per plant found. The percentage of prussic acid at the time of the second analysis was in general only about one hundredth of what it had been thirty-eight days before. This rapid diminution in the percentage of prussic acid in the growing plants makes it imperative in most cases to compare only plants of the same *age*. It is possible that due to the irregular distribution of the nitrate on the ground, some of the plants that show unduly large amounts of prussic acid may have grown on spots where lumps of nitrate fell.

The analyses of September 4 (table 4) agree with the earlier ones (tables 2 and 3) in showing that there is more prussic acid in plants that were given

TABLE 5

Percentage and amount per plant of hydrocyanic acid found in sorghum plants at different ages

PLOT	NITRATE APPLIED PER ACRE	HCN CONTENT AT END OF VARIOUS INTERVALS AFTER SEEDING					
		17 days		55 days		88 days	
	lbs.	per cent	mgm.	per cent	mgm.	per cent	mgm.
				Site I			
1	None	0.3000	0.465	0.0035	0.210	Trace	Trace
2	200	0.2700	0.628	0.0045	0.856	0.00029	0.033
3	400	0.2800	0.528	0.0079	1.975	0.00027	0.083
4	800	0.5000	0.926	0.0063	1.675	0.00330	0.924
5	1600	0.4200	0.840	0.0077	2.002	0.00320	0.864
				Site II			
6	None	0.3000	1.470	0.0040	0.720	0.00180	0.468
7	200	0.5000	1.610	0.0040	0.800	0.00310	1.116
8	400	0.5300	1.390	0.0065	1.105	0.00250	0.800
9	800	0.3900	0.910	0.0078	3.280	0.00190	1.102
10	1600	0.5400	1.080	0.0078	1.950	0.00340	1.564

nitrate than in the unfertilized ones, but the amount is only roughly in proportion to the amount of nitrate applied.

A comparison from tables 2, 3, and 4 is given in table 5. The data show that the percentage of hydrocyanic acid was greatest in very young plants and less at each succeeding sampling. From tables 3 and 4 it will be seen that the percentage of prussic acid was much greater in the leaf than in the stem and that it varied more in the leaf. The total amount per plant varied, in general, as the nitrate applied. On the unfertilized plots it diminished from first to last, but on six of the eight fertilized, it first increased, and later decreased.

Up to the September sampling, care had been taken that the samples analyzed should all be from the interior of the plots, in order to avoid the effect of applications on adjoining plots. At this sampling the plants along

the margin of the plots, where they had more room, and more especially along the margin of the no-nitrate plot, were larger and greener than those in the interior of the same plot. Such is usually the case when any crop is planted thickly enough to be crowded. It was to be expected that these differences were due to a more liberal supply of water or of nitrate or of both. The earlier results of these experiments suggested that the difference in nitrate would be reflected in a greater amount of prussic acid in the plants that grew along the margin and such was the result found by analysis (table 6, site I).

TABLE 6

Hydrocyanic acid found September 6 in sorghum from margin and interior of University Farm plots

SOURCE OF SAMPLE		HEIGHT	AVERAGE WEIGHT PER PLANT	HYDROCYANIC ACID FOUND			
				Leaf	Stem	Whole plant	Per whole plant
		inches	*gm.*	*per cent*	*per cent*	*per cent*	*mgm.*
Site I {	Margin...................	52	50	0.00230	0.00160	0.00184	0.920
	interior.................	52	52	Trace	0.00180	0.00137	0.712
Site II {	margin...................	70	126	0.00550	0.00140	0.00180	2.268
	interior.................	48	20	0.00830	0.00120	0.00376	0.752

SAMPLES FROM FIELDS ON OTHER FARMS

This result in turn suggested the analysis of similar pairs of samples from fields other than on University Farm, wherever they showed similar differences in growth and color. Several pairs were secured and analyzed, but none were grown under conditions that even approximate those sought. No fields were found where the sorghum had been sown broadcast, nor in drills close together, as on the plots on University Farm, so as to make the crowding and the resulting competition for nitrate severe.

On all, the sorghum had been planted in rows, 30 inches to 36 inches apart, and kept clean cultivated. The crowding, even where the plants were thickest, was far less pronounced than on the plots at University Farm, and accordingly the plants were in general taller, and much more stocky. In several fields examined, the plants at the margin instead of being more thrifty than in the interior were less so, due to weeds or grass, or in some cases to shade from adjoining groves or orchards. Such were avoided, though where the lack of vigor is due to competition for nitrate, the results should be the same as where the plants at the margin are more vigorous than those in the interior.

There was no clear evidence of nitrogen hunger in any case. Even the samples secured from the Anoka sandy field, which were rather yellowish in color, may have been suffering quite as much from lack of water as from nitrogen hunger.

The analyses indicate the range in hydrocyanic acid that may be expected on average farms, where the sorghum has been given plenty of room and good cultivation but no nitrate, and is approaching maturity.

TABLE 7

Hydrocyanic acid found in sorghum from various fields

Grown in rows and kept clean cultivated, but not fertilized. In each case sample *b* is from the thicker stand.

SOURCE OF SAMPLE		HEIGHT	AVERAGE WEIGHT PER PLANT	HYDROCYANIC ACID FOUND			
				Leaf	Stem	Whole plant	Per whole plant
		inches	*gm.*	*per cent*	*per cent*	*per cent*	*mgm.*
III. Anoka Co	a	48	51	0.00042	0.00012	0.00017	0.087
	b	40	24	0.00100	0.00042	0.00055	0.132
VII. Hennepin Co	a	50	57	0.01660	0.00070	0.00340	1.938
	b	52	43	0.00130	0.00050	0.00060	0.258
VIII. Hennepin Co	a	69	92	0.01380	0.00060	0.00360	3.313
	b	68	97	0.01010	0.00190	0.00260	2.522
IX. Hennepin Co	a	70	96	0.01110	Trace	0.00270	2.592
	b	70	98	0.00960	Trace	0.00230	2.254
V. Hennepin Co	a	..	73	0.00086	0.00018	0.00028	2.044
	b	..	44	Trace	None	Trace	Trace

TABLE 8

Hydrocyanic acid found in sorghum plants near or upon peat compared with those not so situated

SOURCE OF SAMPLE	HEIGHT	AVERAGE WEIGHT PER PLANT	HYDROCYANIC ACID FOUND			
			Leaf	Stem	Whole plant	Per whole plant
	inches	*gm.*	*per cent*	*per cent*	*per cent*	*mgm.*
VI. Hennepin County, a	100	163	0.00490	0.00260	0.00310	5.053
X. Hennepin County, b	50	73	0.00990	0.00200	0.00370	2.701
IV. Ramsey County, c	...	135	0.01330	0.00120	0.00580	7.830
XI. Ramsey County, d	...	103	0.00880	0.00220	0.00360	3.708

a. Peat soil covered with about twelve inches of sandy loam.
b. Dark sandy loam fifty feet from VI.
c. About six feet from edge of bog.
d. About twelve feet from edge of bog.

SUMMARY

1. Analyses for hydrocyanic acid were made at three stages of growth, 17 days, 55 days, and 88 days after seeding, in the case of sorghum grown on plots on two productive fields, both without added nitrate, and with various amounts applied shortly after the young plants appeared.

2. At the first stage the plants from all the plots contained a very high percentage of hydrocyanic acid, which was highest in those from the fertilized plots.

3. At the second stage the plants on all the plots given nitrate were larger and of a darker green color than on the unfertilized plots, while they also carried a higher percentage and larger amount per plant of hydrocyanic acid.

4. At the third stage the effect of the added nitrate was still more marked both in the percentage of hydrocyanic acid and in the amount per plant.

5. The data from the three stages of growth show that the percentage of hydrocyanic acid diminished from first to last, and that at all stages it was greater on the fertilized than on the unfertilized plots. The amount per plant on the unfertilized plots decreased from first to last, while on the fertilized plots it first increased and later decreased.

6. Since the percentage of hydrocyanic acid in the leaves usually leads to the same conclusion as that in the whole plants, it may sometimes suffice to analyze the leaves only in the case of older plants. Usually the total weight per plant appears the more trustworthy basis for comparison, but it is still better to report both the percentage and the amount per plant.

REFERENCE

(1) PINCKNEY, R. M., 1924. Effect of nitrate applications upon the hydrocyanic acid content of sorghum. *In* Jour. Agr. Res. (soon to appear).

PRELIMINARY NOTE ON THE DISTRIBUTION OF NITRATES IN SOIL UNDER CORN CULTURE[1]

A. W. BLAIR AND A. L. PRINCE

New Jersey Agricultural Experiment Stations

The nitrogen availability plots at this station which have been under a five-year rotation of corn, oats (two years), wheat and timothy for the past fifteen years, have already been studied with reference to the nitrate content of the soil, under different nitrogen treatments, and also at different seasons of the year (1).

The corn crop of 1923 offered an opportunity for a study of the nitrate content of the soil in the vicinity of the growing plant (about 4 or 5 inches from the hill) in comparison with the content of the soil in the middle of the row (about 20 or 21 inches from the hill). Unfortunately the work was not started until late in the season and it is therefore not possible, at this time, to report results obtained at different dates throughout the growing season.

The results, representing only one sampling made early in August from a number of plots, are interesting and indicate the need of further study along this line. These plots have received annual applications of fertilizers as follows:

Plot 4. Acid phosphate and muriate of potash.

Plot 5. Acid phosphate and muriate of potash, plus 16 tons of cow manure.

Plot 7. No fertilizer of any kind.

Plot 9. Acid phosphate, muriate of potash, and nitrate of soda at the rate of 320 pounds per acre.

Plot 11. Acid phosphate, muriate of potash, and ammonium sulfate equivalent to 320 pounds nitrate of soda per acre.

Plot 13. Acid phosphate, muriate of potash, and dried blood equivalent to 320 pounds nitrate of soda per acre.

Plot 17. Acid phosphate, muriate of potash, and rye straw at the rate of 4000 pounds per acre.

Plot 18. Acid phosphate, muriate of potash, and nitrate of soda (as above) plus 16 tons of cow manure per acre.

Plot 19. Acid phosphate and muriate of potash.

The plots of one section designated *A* have not been limed during the entire time, while the plots of the other section designated *B* have received

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liberal applications of lime in the carbonate form at intervals of five years beginning with the corn crop of 1908. The fertilizer treatment has been the same for both sections. Samples of soil were taken by cutting to a depth of about 6⅝ inches, promptly dried and nitrates determined by the phenol-disulfonic acid method. The results of these determinations, in parts of nitrate per million, together with the yields of dry shelled corn in bushels per acre are shown in table 1.

For the unlimed section it is noteworthy that in every case the nitrates are higher in samples taken away from the growing corn than near it, the average for the former being 7.52 parts per million and for the latter 3.31 parts per million. For the limed section there is little difference between samples taken near the corn and away from it, the average for the former being 2.53 and for the latter 2.43 parts per million. In both cases the figures are distinctly lower than the corresponding figures for the unlimed section.

TABLE 1

The distribution of nitrates under corn—unlimed and limed plots

PLOT NUMBER	A. UNLIMED			B. LIMED		
	Shelled corn per acre	Nitrates		Shelled corn per acre	Nitrates	
		Near corn	Away from corn		Near corn	Away from corn
	lbs.	*p.p.m.*	*p.p.m.*	*lbs.*	*p.p.m.*	*p.p.m.*
4	1795	1.18	1.40	2600	1.28	1.44
5	2775	3.60	5.32	2383	.....	....
7	695	0.82	6.78	2248	1.12	1.22
9	·2180	5.27	6.67	2250	1.79	1.28
11	758	1.52	·12.76	2800	1.33	1.68
13	2603	1.28	13.28	2970	1.55	1.63
17	1295	0.88	1.28	2653	1.76	1.76
18	3175	14.40	19.04	3413	10.00	8.80
19	1650	0.80	1.12	2405	1.44	1.60
Average.	1881	3.31	7.52	2636	2.53	2.43

It is possible that a more limited root system may have been the cause of the higher nitrates in soil from the middle of the rows on the unlimed plots. The soil of these plots is distinctly acid, ranging from pH 4.6 to pH 5.6, and this would no doubt limit root development to some extent. An average yield of 1881 pounds of shelled corn per acre on these plots as against 2636 pounds per acre on the limed plots would tend to support this theory. The soil of the limed plots had a pH value of about 6.9–7.2.

The higher nitrate content in the middle of the row could hardly be attributed to the cultivation, since if this were the cause, then the same difference should have been noted on the limed plots (level cultivation was practiced). The larger yields of corn on the limed plots together with fairly close agreement between the nitrates in samples taken near the growing corn and

in the middle of the row, seem to suggest, as pointed out above, a healthier and more uniform root distribution throughout the soil on the limed area.

The high nitrate content found in plots 18A and 18B must be attributed to the heavy application of nitrogenous fertilizers which these plots have received. With heavy applications of manure annually for fifteen years, the soil has become well supplied with organic matter, a part of which is easily nitrifiable. Plots 4A and 19A receive no nitrogen and 17A receives rye straw only, and the low nitrate content of these plots together with the low crop yields indicates little readily nitrifiable organic matter. Plot 11A, although having a pH value of 4.6, shows a high nitrate content in the sample from the middle of the row, which indicates that nitrification was going on even in the presence of high acidity. The fairly high nitrate content of soil from 9A reflects the nitrate of soda treatment for this plot.

Nitrate determinations were also made on samples of soil from two other corn plots which previous to this year had been continuously in soybeans for ten years. One of these, plot M, has been limed at intervals of five years (omitted in 1923) and the other had received no lime during that period. The nitrate results and yields of shelled corn are as follows:

PLOT	SHELLED CORN PER ACRE	NITRATES NEAR CORN	NITRATES AWAY FROM CORN
	lbs.	p.p.m.	p.p.m.
M. Limed...................................	2465	0.92	1.57
N. Not limed................................	308	6.12	13.32

Here as in the previous experiments nitrates are higher in samples taken from the middle of the row than in those taken near the corn. The soil of plot N is very acid, pH 4.6, and as a consequence the corn crop was practically a failure. Thus the small amount of nitrates required for the crop would seem to account for the rather high nitrate content of the soil.

Nitrates were determined in samples from two other corn plots, 65 and 66, both of which received nitrogenous fertilizers and were also limed. The nitrate results and yields of shelled corn were as follows:

PLOT	SHELLED CORN PER ACRE	NITRATES NEAR CORN	NITRATES AWAY FROM CORN
	lbs.	p.p.m.	p.p.m.
65. Limed.................................	3000	0.72	1.13
66. Limed.................................	2925	1.39	4.64

Here also the nitrates are higher in samples taken away from the corn than in those taken near it, but since both plots were limed the explanation given above for the difference does not hold here. However, with one exception it is apparent that the nitrates were being utilized almost up to the limit, and root development was probably normal in both cases.

Definite conclusions should not be drawn until further work is done, but there is good reason to suspect a more complete utilization of the nitrates that are formed in the soil, when the soil reaction is near the neutral point, than when it is distinctly on the acid side.

REFERENCE

(1) BLAIR, A. W., AND PRINCE, A. L. 1922 Variation of nitrate nitrogen and pH values of soils from the nitrogen availability plots. *In* Soil Sci., v. 14, no. 1, p. 9–19

INFLUENCE OF VARYING RATIOS OF PHOSPHORIC ACID AND POTASH ON CROP YIELD AND NITROGEN RECOVERY

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In an earlier paper (1) it was pointed out that a nitrogen, phosphoric acid, potash ratio of 5-10-4 gave a slightly higher yield of barley (grain and straw) than a ratio of either 5-5-4 or 5-15-4. With a second or residual crop of sorghum, doubling and trebling the application of phosphoric acid gave no appreciable increase in yield. Under the same conditions doubling the potash application gave a slight increase in the barley crop but no appreciable increase in the residual crop.

The increased amounts of phosphoric acid and potash had little influence on the percentage of nitrogen and phosphoric acid in the crops. In most cases the higher amounts of phosphoric acid and potash did give somewhat higher nitrogen recoveries. For example, with a ratio of 5-5-4 the recovery of nitrogen from nitrate of soda was 61.2 per cent and with a ratio of 5-15-4 it was 82.3 per cent. With a ratio of 5-5-8 the recovery was 69 per cent and with a ratio of 5-15-8 it was 76.1 per cent.

A higher recovery of nitrogen was obtained when the nitrogen was in the form of nitrate of soda than when in the form of ammonium sulfate, dried blood, or a mixture of the three. Taking the two crops together, the lowest recovery was from ammonium sulfate, with an average of about 45 per cent, the dried blood and the mixture of the three materials standing between this and the nitrate of soda, with an average of a little more than 50 per cent.

RESULTS FOR THE CORN CROP OF 1923

The work which was started in 1922 was continued in 1923 without change in plan. The plan provides for sixty outdoor cylinders having a surface area of three square feet. The soil used is a silt loam which had not been under cultivation for many years and was distinctly acid. To overcome this acidity pulverized limestone was applied to all cylinders in amounts sufficient to bring the reaction to about pH 6.6–7.0. In applying the fertilizers, provision is made for nitrogen, phosphoric acid and potash ratios of 5-5-4; 5-10-4 and 5-15-4, and this is repeated with the amount of potash doubled. Nitrogen is used in the form of nitrate of soda, ammonium sulfate, dried blood and a com-

[1] Paper No. 169 of the Journal Series, New Jersey Agricultural Experiment Stations, Department of Soil Chemistry and Bacteriology.

bination of the three. Equivalent amounts of nitrogen are used in all cases. The work is carried out in duplicate.

In the fall of 1922 the soil was prepared and phosphoric acid and potash applied in accordance with the plan (nitrogenous fertilizers were withheld for spring application), and all cylinders were seeded to wheat. On account of winter injury the wheat was treated as a green manure crop and the ground prepared for corn in the spring of 1923. This was planted May 14 and the nitrogenous fertilizers applied in accordance with the plan. Phosphoric acid and potash were not applied at this time. The corn was planted thick to be harvested as forage and not as a mature crop. Growth through the season was normal and the corn was harvested August 16. This was thoroughly dried, weighed and samples prepared for analysis. The yields of dry matter and percentage of nitrogen and nitrogen recovered, for the various treatments, are shown in table 1.

Attention may be called to the fact that a larger average yield was obtained with the 5-10-4 ratio than with either the 5-5-4 or the 5-15-4; likewise the 5-10-8 ratio gave a larger yield than the 5-5-8 or the 5-15-8. It would thus appear that for the soil and crop in question, at least, an amount of phosphoric acid equal to twice the amount of nitrogen used gave better results than when the two were used in equal amounts or when the phosphoric acid was three times the amount of the nitrogen. This is interesting since it is about the ratio which obtains in a number of the high grade fertilizers, especially the potato fertilizers.

A study of the percentage of nitrogen found in the dry matter reveals the fact that this was not influenced by the amount of phosphoric acid used, the figures being practically the same, within the limit of error, for the three different amounts of phosphoric acid. It may be pointed out furthermore that the percentage of nitrogen varies within quite narrow limits—0.45 to 0.50 per cent. Taking the general average, it is found that the percentage of nitrogen is slightly higher with the double than with the single portion of potash, irrespective of the amount of phosphoric acid used.

Evidently the amount of phosphoric acid has had only slight influence on the percentage of nitrogen recovered. The highest average recovery, 34.5 per cent, was with the 5-15-4 ratio, and the next highest average, 32.6 per cent, was with the 5-10-8 ratio. The general average with the single portion of potash is about one point higher than the corresponding figure with the double portion of potash.

The form in which the nitrogen was used has had a far greater influence on the per cent recovered than has the amount of phosphoric acid or potash. For the section with the single portion of potash the average recovery with nitrate of soda was 41 per cent, and with dried blood 22 per cent. The corresponding figures for the section with the double portion of potash are 45.3 and 19 per cent respectively. The recoveries with ammonium sulfate, and with the combination of the three materials, stand between the nitrate of soda and the dried blood.

TABLE 1

Yield of dry matter (corn forage), per cent nitrogen in dry matter, and per cent nitrogen recovered

(N, P₂O₅, and K₂O used in ratios as indicated)

	Ratio 5-5-4			Ratio 5-10-4			Ratio 5-15-4			Average		
	Dry matter	Nitrogen in dry matter	Nitrogen recovered	Dry matter	Nitrogen in dry matter	Nitrogen recovered	Dry matter	Nitrogen in dry matter	Nitrogen recovered	Dry matter	Nitrogen in dry matter	Nitrogen recovered
	gm.	per cent	per cent	gm.	per cent	per cent	gm.	per cent	per cent	gm.	per cent	per cent
A. Check............	140.8	0.462	...	138.6	0.510	...	136.5	0.490	...	138.6	0.488	...
B. Nitrate of soda.......	271.8	0.486	40.6	285.1	0.470	38.4	285.5	0.487	43.9	280.8	0.481	41.0
C. Ammonium sulfate......	240.7	0.478	30.3	235.6	0.470	24.2	249.8	0.475	31.4	242.0	0.474	28.6
D. Dried blood.........	202.3	0.495	21.4	224.8	0.454	19.0	215.0	0.506	25.6	214.0	0.485	22.0
E. ⅓ N from each........	254.0	0.470	33.0	279.8	0.474	37.6	272.1	0.470	37.1	268.6	0.472	35.9
Average.......	*221.9*	*0.478*	*31.3*	*232.8*	*0.477*	*29.8*	*231.8*	*0.486*	*34.5*	*228.8*	*0.480*	*31.9*

	Ratio 5-5-8			Ratio 5-10-8			Ratio 5-15-8			Average		
	Dry matter	Nitrogen in dry matter	Nitrogen recovered	Dry matter	Nitrogen in dry matter	Nitrogen recovered	Dry matter	Nitrogen in dry matter	Nitrogen recovered	Dry matter	Nitrogen in dry matter	Nitrogen recovered
	gm.	per cent	per cent	gm.	per cent	per cent	gm.	per cent	per cent	gm.	per cent	per cent
F. Check............	158.7	0.454	...	156.6	0.454	...	158.4	0.451	...	157.9	0.453	...
G. Nitrate of soda.......	308.5	0.470	44.2	321.0	0.451	44.7	316.3	0.470	46.9	315.3	0.464	45.3
H. Ammonium sulfate......	265.0	0.451	28.7	267.0	0.462	31.8	274.3	0.451	31.7	268.8	0.455	30.7
I. Dried blood.........	217.0	0.467	17.6	239.5	0.443	21.3	213.3	0.474	18.0	223.3	0.462	19.0
J. ⅓ N from each........	241.4	0.454	22.7	269.0	0.464	32.7	263.3	0.454	29.2	257.9	0.457	28.2
Average.......	*238.1*	*0.459*	*28.3*	*250.6*	*0.455*	*32.6*	*245.1*	*0.460*	*31.5*	*244.6*	*0.458*	*30.8*

SUMMARY

Taking the work as a whole, a ratio of 1:2 for nitrogen and phosphoric acid gave somewhat better yields than a ratio of 1:1 or 1:3.

Neither the amount of phosphoric acid used nor the form of nitrogen have perceptibly influenced the percentage of nitrogen in the dry matter.

The form of nitrogen has on the other hand had a very pronounced influence on the crop yields and consequently on the percentage of nitrogen recovered in the crop. With nitrate of soda the recovery was, on an average, about 43 per cent; with ammonium sulfate it was close to 30 per cent and with dried blood a little over 20 per cent. When the nitrogen was taken from three sources (one-third from each) the recovery was, on the average, slightly better than with ammonium sulfate alone.

The recovery calculated on the basis of two crops, as in the case of 1922, is higher than with one crop only. This undoubtedly means a conservation of nitrogen, since much of what was taken up by the second crop would otherwise have been lost.

REFERENCE

(1) LIPMAN, J. G., AND BLAIR, A. W. 1923 The influence of varying ratios of phosphoric acid and potash on the yield, and on the nitrogen and phosphoric acid content of the crop, with different nitrogenous materials. *In* N. J. Agr. Exp. Sta. 44th Ann. Rpt. (soon to appear).

PLATE 1

NITRATE OF SODA WITH SINGLE AND DOUBLE PORTION OF POTASH

FIG. 1. TWO CYLINDERS UNDER SERIES A, NO NITROGEN; CYLINDER UNDER SERIES B,
NITROGEN FROM NITRATE OF SODA

Ratio 5–15–4

FIG. 2. CYLINDER UNDER SERIES F, NO NITROGEN; TWO CYLINDERS UNDER SERIES G,
NITROGEN FROM NITRATE OF SODA

Ratio 5–15–8

NITRATES AND NITRIFICATION IN FIELD SOILS[1]

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The subject of nitrification in soil has been the theme of considerable investigation during the last thirty years and much information regarding the process has been accumulated. It has come to be quite generally recognized that there are certain conditions in the soil which to a large extent control the production of nitrates, or regulate the so-called nitrifying power. Thus it is believed that the requirements for the best nitrification in any soil include optimum moisture, plenty of easily decomposable organic matter, a basic reaction, good tilth, and the presence of available phosphorus and potassium. These are also the chief requirements for good crop yields and hence it would seem that there should be a relationship between the nitrates in soils or their nitrifying power and crop yields.

According to Brown (4) there is a rather close relation between bacterial activities and the crop-producing power of soils. Vogel's experiments (16) with potatoes and barley indicated that the productiveness of the soil was in direct relation to the nitrifying capacity. Burgess (5) considers nitrification by far the most accurate biological soil test for predicting the probable fertility of Hawaiian soils. But Jensen (8) thinks that the differences in the average seasonal accumulations of nitrates could not have been due entirely to the differences in yields of beets on the soils which he studied.

King and Whitson (9), Stewart and Greaves (15), Russel (14), Albrecht (1), and Whiting and Schoonover (20) found that the period of loss in nitrate content in soil in the summer coincided with the period of rapid growth of crops. Many investigators (9), (13), (7), (8) (14), (1), (20) have found that the greatest nitrification takes place in soil in the late spring and early summer. Several found an increase in nitrate content in the early autumn, following a period of low content in the late summer. Vogel (16), however, obtained the greatest nitrification in October and November and concluded that the treatment of the soil had less effect upon nitrification than the time of year. Lemmerman and Wichers (10) concluded that there is not sufficient evidence to show a direct periodic influence of the time of year on the life activities of the organisms and they believe that the physical factors control the process.

There seems to be no doubt that nitrification is affected very materially be variations in moisture content and investigations have placed the optimum at different points, ranging from 50 per cent up to 60 per cent saturation. The effects of manure, lime and phosphates on nitrification have been studied quite frequently and while the results vary considerably depending upon the conditions of the experiments and probably mainly upon the soil types used

in the tests, it has generally been found that these fertilizers give distinct and often large increases in the production of nitrates, and in the nitrifying power of the soil. The experiments of Warington (17), Withers (18), Brown (2), (3), Whiting and Schoonover (20), Noyes and Conner (12), Vogel (16), Jensen (8), White (19), and Fraps (6) give typical results with these fertilizers. Negative results have sometimes been secured as indicated in the work of Fraps (6), Vogel (16) and MacKenna (11), but these are exceptional cases.

EXPERIMENTAL

The purpose of the experiments reported here was to determine the effect of seasonal conditions, moisture content and various fertilizer treatments on

TABLE 1
Treatment of plots

PLOT NUMBER	TREATMENT
1300	Check
1301	1600 lbs. manure
1302	400 lbs. manure (annually)
1303	1600 lbs. manure + lime
1304	2400 lbs. manure + lime
1305	Check
1306	3200 lbs. manure + lime
1307	4000 lbs. manure + lime
1308	1600 lbs. manure + 200 lbs. raw rock phos. + lime
1311	1600 lbs. manure + 20 lbs. acid phosphate (ann.) + lime
1312	1600 lbs. manure + 200 lbs. raw rock phos. + 20 lbs. KCl (ann.) +lime
1313	1600 lbs. manure + 30 lbs. 2–8–2 (ann.) + lime
1314	1600 lbs. manure + 30 lbs. 2–12–5 (ann.) + lime
1315	Check
1324	Crop residues
1325	Check
1326	Crop residues + lime
1328	Crop residues + 200 lbs. raw rock phos. + lime
1331	Crop residues + 20 lbs. acid phosphate (ann.) + lime
1332	Crop residues + 30 lbs. 2–8–2 (ann.) + lime
1333	Crop residues + 200 lbs. raw rock phos. + 20 lbs. KCl (ann.) + lime
1334	Crop residues + 30 lbs. 2–12–5 (ann.) + lime.
1335	Check

the nitrate content and the nitrifying power of an Iowa soil and to ascertain if there is any relation to crop yields.

The experiment was carried out on some of the 36 plots in the 1300 series on the agronomy farm of the Iowa Agricultural Experiment Station. These plots are one-tenth of an acre in size, separated by division strips and surrounded by borders in the usual way and they have been under experiment for the past seven years. They are located on the Webster silty clay loam soil type, which is fairly uniform, but contains very small spots of the silt

loam and loam of the same series and of the Carrington loam and Clarion loam. The type is about as uniform as it occurs throughout the Wisconsin drift soil area.

The treatments to which these plots have been subjected are shown in table 1. A four-year rotation is practised and unless otherwise stated the treatments are made once in four years. In the year of this investigation

TABLE 2

Moisture determinations in soils

PLOT NUMBER	JUNE 21	JULY 25	AUGUST 9	AUGUST 30	SEPTEMBER 20*	SEPTEMBER 23	OCTOBER 12	AVERAGE
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
1300	17.5	7.5	6.5	12.5	20.0	17.5	16.0	13.9
1301	17.2	7.5	7.5	14.0	20.0	17.5	15.0	14.1
1302	15.0	13.5	6.5	13.0	20.0	17.5	18.0	14.7
1303	15.5	10.0	6.0	15.0	20.0	17.5	18.0	14.6
1304	17.0	9.0	7.5	12.5	20.0	17.5	18.0	14.5
1305	16.0	13.5	9.0	16.5	22.5	17.5	18.0	16.1
1306	14.5	12.5	10.0	16.5	22.5	20.0	21.0	16.7
1307	17.5	12.5	10.0	17.5	22.5	22.5	23.5	18.0
1308	17.5	15.0	14.0	17.5	20.0	22.5	20.0	18.1
1311	19.0	15.0	14.0	19.0	25.0	22.5	26.0	20.1
1312	19.0	15.0	16.5	17.5	20.0	20.0	25.0	19.0
1313	22.5	16.5	14.0	17.5	25.0	20.0	26.0	21.2
1314	22.2	18.5	17.5	21.0	25.0	27.5	27.5	22.8
1315	24.0	20.0	15.0	20.0	26.0	25.0	27.5	22.5
1324	17.5	12.5	11.0	15.0	20.5	20.0	20.0	16.5
1325	....	....	....	19.0	16.0	20.0	21.5	19.1
1326	14.0	11.5	13.0	19.0	20.0	17.5	26.0	17.3
1328	20.0	10.5	10.5	19.0	20.0	22.5	23.0	17.9
1331	19.5	16.5	12.5	18.5	25.0	25.0	20.0	19.5
1332	23.7	19.0	15.0	16.0	31.5	27.5	23.0	22.3
1333	21.2	19.0	11.5	17.0	25.0	25.0	18.0	18.1
1334	17.5	11.0	6.0	10.0	25.0	25.0	17.0	15.9
1335	15.5	10.0	5.0	9.0	25.0	20.0	13.0	13.9
Av.	18.3	12.5	10.8	16.2	22.5	21.2	21.0	

* Rained the previous day.

the plots were in corn. Clover had been grown in the preceding season and on plots 1324 to 1334 inclusive, the second cutting of clover was turned under for the residue treatment.

Eight samplings were made from these plots from June to October, each sample being taken from a different place in the plots. The surface soil was removed from an area two feet square and with a sterile trowel the soil in that area, to a depth of seven inches, was throughly mixed and the sample

was then drawn. Moisture determinations were made on all samples and the results are given in table 2. Nitrate determinations were made by the phenoldisulfonic acid method and the nitrifying power of the soils was determined by the beaker method using ammonium sulfate. The incubation period in the latter determination was four weeks at room temperature.

The nitrate content of the soils at the different samplings is shown in table 3. The highest amount in almost all cases was found in the samplings made in June. There was a gradual decrease during the next month and from then on the decrease was very rapid until the middle of September, when the amount of nitrate reached a minimum. Later a decided rise in the nitrate content occurred, as noted by others.

Comparing these results with those given for moisture in table 2, it seems that the most nitrates were present when the moisture content was about 18 per cent. The average moisture content for the whole field was about 18 per cent on June 21 when the nitrate content was the highest. Plots 1307, 1308, 1326 and 1328 which had a high nitrate content for the entire season had an average moisture content of about 18 per cent. Plots 1301, 1302 and 1304 which also contained considerable nitrates had an average moisture content of only 14 to 15 per cent but in general the best results were secured with the higher per cent. The results obtained on August 9 are significant. The rapid decrease in the nitrate content on that date coincided with the decrease in the moisture content which averaged 11 per cent for the whole series. This would indicate that the influence of the time of the year on nitrification is due particularly to high or low rainfall. Plot 1335 which throughout the season had in general a higher amount of nitrate than the adjacent plots 1334 and 1333 showed smaller amounts on August 9 and 30 when its moisture content was also lower. A comparison of the nitrates in the soils on September 20 and 23 is of interest. There was a heavy rainfall on September 19 and its effect is shown in the smaller amounts of nitrates on the next day.

Considering the effect of fertilization, it is evident that the addition of 8 tons of manure once in four years (plot 1301) or in four annual applications (plot 1302) caused an increase of about 60 per cent over plot 1305 in the nitrate content. The 12-ton application (plot 1304) caused a still greater increase in nitrates. Applications of manure larger than 12 tons did not cause as large increases.

The results on plot 1303 receiving 8 tons of manure cannot be explained with the data at hand. Evidently some unknown factor came into play there.

The year previous to this investigation plots 1324–1335 were in clover and the second cutting was turned under in the fall. Plot 1326 which received lime beside the clover turned under showed a 50 per cent increase in nitrates over the check plot 1325. In plot 1324 which received clover but no lime, nitrification was depressed. Probably the acids produced by the

decomposing green manure were not neutralized and therefore had an adverse effect on the nitrifying organisms.

Among the mineral fertilizer treatments rock phosphate (plots 1308 and 1328) resulted in the largest increase in nitrate nitrogen.

Table 4 shows the nitrifying power of the soils or their ability to serve as a medium for the growth of nitrifying organisms. The extent of the growth of nitrifying organisms is measured by the amount of $(NH_4)_2SO_4$ oxidized in a given period under optimum conditions of moisture and temperature.

TABLE 3

Pounds per acre of nitrate nitrogen in the surface soil in corn plots

PLOT NUMBER	JUNE 21	JULY 25	AUGUST 9	AUGUST 30	SEPTEMBER 20	SEPTEMBER 23	OCTOBER 12	AVERAGE
1300	77.62	56.04	22.84	16.18	11.78	10.42	15.24	30.02
1301	68.74	49.22	25.68	23.26	12.20	22.04	17.40	31.22
1302	67.52	81.30	24.98	12.84	8.18	7.76	16.34	31.28
1303	55.66	39.82	22.56	14.70	14.70	7.42	16.34	23.52
1304	90.50	45.88	21.88	14.98	11.50	10.76	22.94	34.06
1305	52.48	31.62	14.00	12.46	7.54	7.46	11.94	19.64
1306	46.88	36.58	15.02	19.74	8.06	6.78	18.74	21.74
1307	54.04	34.84	16.00	19.78	11.68	12 00	17.78	25.14
1308	45.82	42.26	20.66	22.58	7.96	8.04	24.00	24.48
1311	49.02	29.74	16.66	8.50	11.21	10.80	12.44	19.78
1312	41.98	48.92	18.78	11.06	8.06	12.20	17.34	22.65
1313	64.88	57.98	22.98	26.86	10.34	22.72	13.40	31.30
1314	95.70	32.68	20.78	16.30	11.74	12.40	22.34	30.26
1315	68.90	71.00	26.44	21.50	11.86	15.90	21.52	33.88
1324	32.78	22.22	13.12	11.60	8.00	11.10	15.76	16.38
1325				25.58	6.82	12.98	13.76	14.78
1326	50.56	46.10	13.04	18.48	7.28	11.98	18.66	23.72
1328	74.10	38.08	11.26	11.26	8.86	8.48	12.78	23.60
1331	49.04	36.78	18.48	13.48	9.44	6.58	11.50	20.76
1332	63.18	19.36	20.04	7.72	10.52	7.88	12.20	20.12
1333	51.66	27.16	11.58	9.14	7.62	8.20	10.98	18.04
1334	57.62	36.76	10.32	8.54	6.80	11.84	14.20	20.98
1335	79.90	40.34	9.52	7.40	11.60	10.88	12.20	24.54
Av.	61.28	44.02	16.98	16.88	10.32	12.28	17.42	

In general it is apparent that all the plots receiving treatments showed a higher nitrifying power than the untreated plots. The manure treatments up to 12 tons per acre caused large increases in nitrifying power. Sixteen- and twenty-ton applications caused small increases. The plots receiving crop residues together with mineral fertilizers showed the maximum nitrifying power. The plots receiving acid phosphate were higher in nitrifying power than those receiving rock phosphate. The more even distribution of the

acid phosphate in the soil may account for greater bacterial growth, but probably the solubility of the phosphorus is the more important factor.

In table 5, column 2 gives actual corn yield for 1921; column 3 gives calculated yields for all plots if they were untreated. This calculation is based on the assumption that there is a gradual variation in the natural productiveness of the soil. According to the yields of check plots 1305 and 1315 there is a progressive reduction in the natural productiveness of these and the in-

TABLE 4

The nitrification of $(NH_4)_2SO_4$ calculated as pounds per acre of nitrate nitrogen in the surface soil in corn plots variously treated

PLOT NUMBER	JUNE 21	JULY 12	JULY 25	AUGUST 9	AUGUST 20	SEPTEMBER 20	SEPTEMBER 22	OCTOBER 12	AVERAGE
1300	532.4	443.6	276.2	426.8	351.6	763.6	299.2	315.2	426.0
1301	514.8	474.4	286.0	498.8	332.6	441.2	401.8	314.8	408.0
1302	380.4	454.8	344.8	414.0	374.0	569.6	398.8	337.8	408.0
1303	406.2	456.2	330.8	440.4	364.2	288.0	314.8	210.0	351.4
1304	575.4	454.0	328.0	456.6	297.0	531.0	341.6	167.4	393.8
1305	427.2	405.0	296.0	329.6	321.9	226.6	204.8	131.4	292.8
1306	504.6	438.2	318.0	404.0	333.4	326.0	359.8	134.4	341.0
1307	491.6	554.0	291.4	325.4	293.0	609.2	281.6	192.2	379.8
1308	513.4	430.4	293.0	489.8	360.0	467.6	259.8	269.4	385.4
1311	578.6	465.4	370.6	489.8	231.0	824.0	399.0	294.8	481.6
1312	472.6	484.2	313.4	504.4	408.0	756.8	365.8	343.0	456.0
1313	607.0	523.6	352.0	498.0	352.6	844.4	392.8	313.8	485.6
1314	566.4	493.6	279.8	421.0	383.4	872.8	414.2	301.0	466.6
1315	697.2	512.4	290.2	448.2	398.0	794.6	375.4	132.6	456.0
1324	336.0	444.4	218.0	379.6	309.4	277.8	252.6	187.6	300.6
1325					274.0	311.8	233.0	125.6	236.1
1326	395.6	335.6	219.6	379.4	294.8	400.0	305.8	118.0	306.1
1328	384.6	394.6	233.2	442.4	370.4	455.8	225.8	326.8	366.6
1331	534.4	502.0	306.0	377.2	310.2	826.6	375.4	290.2	440.2
1332	608.2	505.8	262.0	487.0	289.2	858.4	390.4	249.4	456.2
1333	528.8	434.0	260.0	404.0	265.0	923.2	390.2	168.8	421.8
1334	406.4	483.8	230.0	398.8	318.4	276.4	251.4	170.0	304.9
1335	384.8	395.4	193.2	476.8	154.0	311.6	281.8	129.2	290.8
Av.	496.6	453.8	286.0	432.0	329.8	562.6	326.0	227.0	

tervening plots. The difference of 900 lbs. in yield between these plots is therefore evenly distributed over all the plots in between. Similarly with the gradual increase from plot 1315 to 1325 and from 1325 to 1335. Column 4 gives the difference between columns 2 and 3 or the increase due to treatment over the calculated unaided yield. In column 5 the same is expressed in percentages. Up to and including 20 tons, the larger the amount of manure applied the greater was the crop yield obtained. The 20-ton

application effected an increase of 35 per cent and the 16-ton application, a 21.5 per cent increase while 12- and 8-ton applications resulted in increases of 14.9 and 6.4 per cent respectively. It would appear from this that the 20-ton application was the most efficient.

In the manure plots, rock phosphate with potassium caused as large an increase in crop yield as did acid phosphate. In the crop residue plots rock phosphate alone caused as large an increase as acid phosphate.

TABLE 5

Corn yields

PLOT NUMBER	CORN YIELD 1921 PER ACRE	CALCULATED YIELD*	INCREASE DUE TO TREATMENT	
	lbs.	*lbs.*	*lbs.*	*per cent*
1300	4700	4700	....	....
1301	5000	4700	300	6.383
1302	4800	4700	100	2.127
1303	4800	4700	100	2.127
1304	5400	4700	700	14.89
1305	4700	4700	....	......
1306	5600	4610	990	21.47
1307	6100	4520	1580	34.96
1308	5400	4430	970	41.90
1311	5600	4160	1440	34.61
1312	5500	4070	1430	35.14
1313	5600	3980	1520	38.19
1314	6000	3890	2110	53.99
1315	3800	3800	....	......
1324	4190	3932	258	6.531
1325	3920	3920	....	......
1326	4080	3961	119	3.004
1328	4430	4043	387	9.572
1331	4590	4166	424	10.181
1332	4460	4207	253	6.015
1333	4490	4248	242	5.695
1334	4640	4289	351	8.164
1335	4330	4330	....	......

*As if all plots were untreated.

Commercial fertilizers applied with manure resulted in the largest increases in crop yield of all treatments. With crop residues, however, the effect of commercial fertilizers was not marked. Crop residues alone in the case of plot 1324 caused almost as great an increase in crop yield as plots 1332 and 1334 which received commercial fertilizers along with crop residues.

Figure 1 shows graphically the percentage increase or decrease in nitrate content, nitrifying power, and the crop yield (1921) induced by the treatments. The figures for nitrates and nitrifying power represent averages of the results obtained from seven samplings.

The curves for plots 1301, 1302, 1304, 1326 and 1328 indicate that the crop yield was proportional to the nitrate content. The curves for plots 1306, 1307, 1308, 1311, 1312 and 1314 apparently contradict the above statement but in reality they do not. The large increase in crop yield drew heavily on the nitrate content and hence the low nitrate content obtained.

The nitrate content of the soils seems to be proportional to their nitrifying power. This is indicated clearly in the curves for plots 1301, 1302, 1304, 1306, 1307, 1308, 1326 and 1328. The apparent discrepancy between plots 1311 and 1312 is explained as before by the factor of high crop yield and in plots 1331 and 1332 the high nitrifying power and low nitrate content is explained by the high moisture content during the period of sampling which
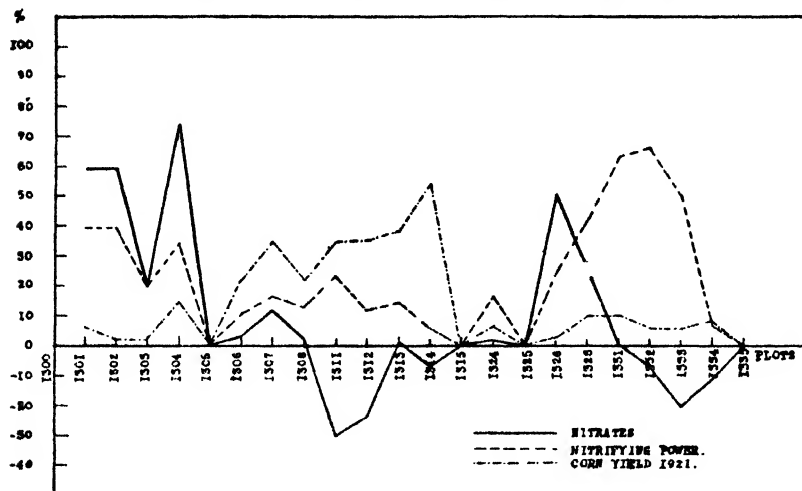
FIG. 1. INCREASE IN NITRATES, NITRIFYING POWER AND CORN YIELD DUE TO TREATMENT

has leached some of the nitrates, also by the fact that the crop yield on these plots was higher than on the check plot.

SUMMARY

1. In all the plots examined there was a large accumulation of nitrates in June with a gradual decrease in July, and a rapid decrease in August and September when it reached the minimum. In October there was a slight increase in nitrates.

2. The optimum moisture content for nitrification in this field soil was about 18 per cent.

3. The application of manure up to 12 tons per acre caused the greatest increase in nitrate accumulation and nitrifying power over the untreated soil. Sixteen- and twenty-ton applications caused smaller increases than those secured when 12 tons per acre were added.

4. The largest application of manure, 20 tons per acre, effected the greatest increase in crop yield in 1921 which was 35 per cent over the untreated plot. The 16-ton application caused an increase of 21 per cent over the untreated plot, the 12-ton application, 15 per cent; and 8-ton application, 6.4 per cent.

5. The crop residues turned under the previous fall increased the nitrate content of the soil when lime was present. The increase in nitrifying power due to the crop residues was also large. Crop residues increased the crop yield 6.5 per cent over the check.

6. Rock phosphate caused greater accumulation of nitrates in the soil than did either acid phosphate or commercial fertilizers. Rock phosphate with crop residues resulted in about as large an increase in crop yield as did acid phosphate.

7. Acid phosphate increased the nitrifying power of the soil more than the rock phosphate did.

8. Complete commercial fertilizers along with crop residues did not affect any greater increase in crop yield than did the crop residues alone.

9. The crop yield on this soil had a direct relation to the nitrate content and to the nitrifying power of the soil.

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SOIL VARIABILITY AS DETERMINED BY STATISTICAL METHODS[1]

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INTRODUCTION

It is recognized by most investigators that the soil constituents are variable for any given area. In the past, several methods have been used in sampling soil for chemical analysis. Probably the most common method was the use of a composite sample taken from any given area. This method may give a fairly uniform sample, but fails to show the soil variability. The object of this paper was to determine, if possible, the variability of nitrogen in the soil, thereby giving one a closer check on fertility experiments.

REVIEW OF LITERATURE

Literature on the subject of soil variability and the probable error in sampling soil for chemical analysis is very limited. Most writers acknowledge the fact that single samples from any given area are of little value experimentally.

Russell (8) recommends 1 to 8 borings, depending on the uniformity of the soil to be tested. Hopkins and Pettit (6) advise the taking of borings from twenty or more places a few rods apart, and to mix thoroughly and use as a composite sample. Bear and Slater (4) compiled the methods used at the New York, Illinois and Wisconsin stations and recommend the following composite samples: $A = 0$ to $6\frac{2}{3}$ inches, $B = 6\frac{2}{3}$ to 20 inches, and $C = 20$ to 40 inches; with 20 to 30 borings for A, and 10 to 15 borings for B and C. This would give good representative samples, but does not show the soil variability of the area sampled. Bear and McClure (3) recommend a 20-sample composite for a $\frac{1}{20}$ acre plot to a depth of 12 inches as giving a very uniform sample.

Robinson and Lloyd (7) determined the probable error in sampling soil for soil survey purposes and concluded that as a general rule the field error for chemical analysis is ±10 per cent, and for mechanical analysis is ±5 per cent. By making six determinations on a single sample of soil, they obtained a laboratory error of ±2.5 per cent. They believe that for soil survey purposes, six borings for a composite sample are satisfactory, where two analyses are made on the sample. Pfeffer and Blanck of Germany, cited by Robinson and Lloyd (7) in working on the nitrogen content of an experimental field, obtained a field error of 2.5 per cent. This, however, was only over a small area or plot. Waynick (9), in making a statistical study on nitrification, states that it is generally conceded among soil investigators that different samples of the same soil type from a comparatively limited area may show considerable

variation among themselves if we apply quantitative measurements to the various constituents of the soil mass. Eighty-one surface and subsurface samples of soil were taken and analyzed individually for nitrate, giving a field error of ± 1.5 per cent for surface and ± 3.1 per cent for the subsurface samples, this probable error being due to soil variability and field
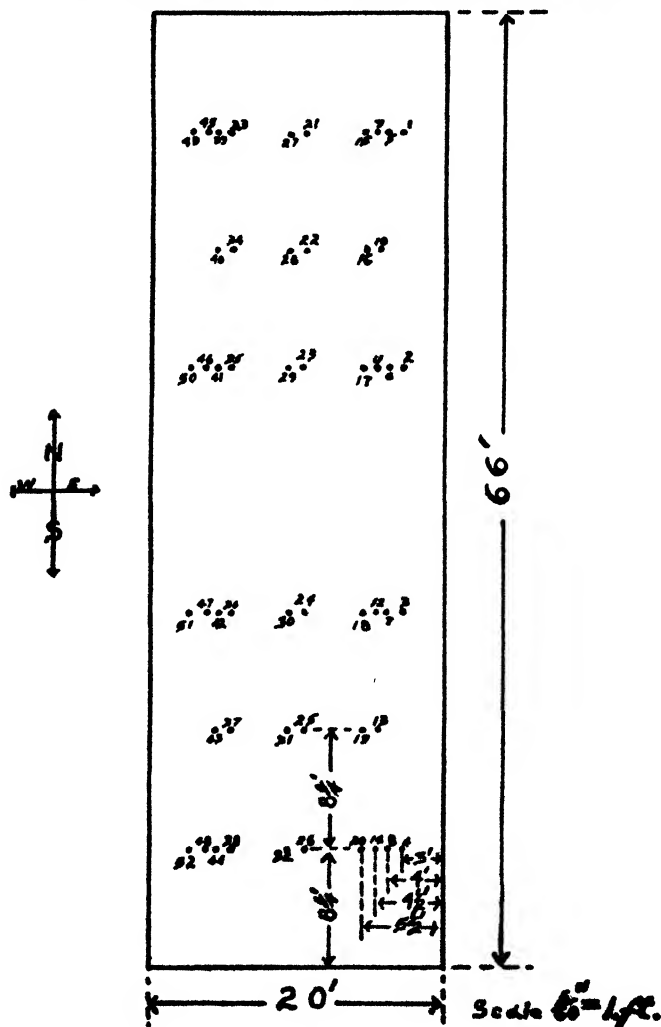
FIG. 1. DIMENSIONS AND LOCATION OF BORINGS ON PLOTS SAMPLED

sampling. Waynick concludes that a composite sample may be considered of value only after the probable error to which it is subject is known, and this can only be determined by the use of a large number of individual samples. Waynick and Sharp (10), in another paper, deter-

mined the probable error in sampling plots for nitrogen and carbon. One hundred samples were taken from each of the two plots sampled. They determined their laboratory error to be 12 pounds of nitrogen per acre when twenty-five determinations were made, and disregarded the laboratory error when one hundred samples were analyzed. They determined the probable error for one field to be ±0.006 per cent, or 240 pounds of nitrogen per acre foot. By knowing the soil variability and probable error for the 100 samples, it is possible to use composite samples for future studies on these plots.

From the variation in the probable errors cited, one would conclude that the results for one area would not be comparable to other areas.[2]

METHODS

Field sampling

Plots A5 and A6 in field VI at the Washington Experiment Station were selected for this work, each being 20 x 66 feet and containing $\frac{1}{33}$ of an acre. The plots were located on the middle to lower portion of a south slope and were considered fairly uniform Palouse silt loam. Since 1899 these two plots have been treated as follows:

A5. Top dressed with 700 pounds of manure in winter after the wheat is up, winter wheat even years and summer fallow odd years.

A6. Plowed early in the spring, tilled well, with winter wheat odd years and summer fallow even years.

Fifty-two samples were taken from each plot as shown in figure 1, each being a core $1\frac{1}{2}$ inches in diameter by $6\frac{2}{3}$ inches deep, and which has been taken as representative of the plowed soil, which is considered as weighing 2,000,000 pounds per acre to this depth. The samples were placed in pint jars, quickly dried and ground to pass a 60-mesh sieve. They were then dried in an oven at 100°C. for five hours and thoroughly mixed.

Chemical analyses

Nitrogen determinations were made by a modified Gunning-Hibbard (1) method, using 5-gram samples with 25 cc. of H_2SO_4, 7–10 gm. of K_2SO_4 and 0.5 gm. of $CuSO_4$. In most cases it was found necessary to digest the samples 7–8 hours to get the best results. Duplicate determinations were made on each sample as a means of checking the laboratory manipulation.

Mathematical calculations

The mathematical treatment will be taken up and discussed briefly, using the data from table 1. This discussion will be applicable to all of the tables.

The mean (m) is obtained for n determinations by adding all of the determinations and dividing by the number of determinations. The standard deviation (σ) is calculated by squaring each deviation from the mean, adding the squares and dividing the sum by the total number of determinations and taking the square root of the quotient (5, p. 428). If the variates are divided into classes, the deviation of each class from the mean is squared and multiplied by the frequency of the variates in that class. The formulas for both methods are as follows:

$$\sigma = \sqrt{\frac{\Sigma\ x^2}{n}} \text{ or } \sigma = \sqrt{\frac{\Sigma\ x^2 f}{n}}$$

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[2] Since this paper was completed, the author found an article on the "Variability of Nitrates and Total Nitrogen in Soils," by A. L. Prince, 1923, in Soil Science, v. 15, no. 5. Prince made twenty-five determinations on each of three plots and found that in the case of total nitrogen determinations, the coefficient of variability was about 5.5 per cent for each plot, and the probable error of the mean, about ±0.7 per cent in each case.

where Σx^2 is the sum of the squares of the deviations from the mean, and n the number of variates. In the second formula f signifies *frequency*. Substituting from table 1, we have

$$\sigma = \sqrt{\frac{2{,}069{,}071}{52}} = 199.5$$

The coefficient of variability (C.V.) is the percentage ratio between the standard deviation and the mean (5, p 433) or

$$\frac{\sigma}{M} = \text{C.V.}$$

Substituting from table 1,

$$\frac{199.5}{2528} = 7.88$$

The standard deviation and coefficient of variability only show the spread or variation one may expect in any set of determinations. To show the reliability of any set of observations, the probable error must be calculated.

The probable error (2, p. 39–47) is an arbitrary term and denotes the amount that must be added or subtracted from the mean or observed value to obtain the two extreme figures within which there is an even chance that the true value lies. There is an even chance also that it lies without these limits. As one increases or multiplies the probable error, the chances that the observed result will be within the limiting figures increases.

To obtain the probable error of a single variate (P.E.$_s$) the standard deviation is multiplied by the factor 0.6745 (which is a constant used in statistical calculations), the formula (5, p. 698) being

$$(\text{P.E.}_s) = 0.6745 \times \sigma$$

Substituting from table 1,

$$(\text{P.E.}_s) = 0.6745 \times 199.5 = \pm 134.7$$

To determine the probable error of the mean (P.E.$_m$) of n variates, divide the probable error of a single variate by the square root of the number of variates (5, p. 440) or

$$\text{P.E.}_m = \frac{\text{P.E.}_s}{\sqrt{n}} = \frac{0.6745\ \sigma}{\sqrt{n}}$$

Substituting from table 1,

$$\text{P.E.}_m = \frac{0.6745 \times 199.5}{\sqrt{52}} = \pm 18.7$$

This formula shows the weight which numbers have when calculating probable errors. Figure 2 shows graphically how the probable errors decrease or increase when the number is varied.

In figuring the above constants, it is customary to give the probable error in the constants. To determine the probable error in the standard deviation (P.E.$_\sigma$) the following formula (5, p. 440) was used.

$$\text{P.E.}_\sigma = \frac{0.6745\ \sigma}{\sqrt{2n}}$$

Substituting from table 1,

$$\text{P E.}_\sigma = \frac{0.6745 \times 199.5}{\sqrt{2 \times 52}} = \pm 13.2$$

Thus the probable error in the standard deviation for plot 5A is ±13.2 pounds, this error being less than the probable error of the mean, because the number of variates is doubled.

When the coefficient of variability is less than 10 per cent, the approximate probable error is found by multiplying the constant 0.6745 by the coefficient of variability (C.V.), and divid-•ing the product by the square root of twice the number of variates (5, p. 441), giving the formula

$$P.E._{(cv)} = \frac{0.6745 \ C.V.}{\sqrt{2n}}$$

Substituting from table 1,

$$P.E._{(cv)} = \frac{0.6745 \times 7.88}{\sqrt{2 \times 52}} = \pm 0.52$$

When the coefficient of variability is greater than 10 per cent, the more complicated formula (5, p. 441) is used:

$$P.E._{(cv)} = \frac{0.6745 \ C.V.}{\sqrt{2n}} \left[1 + 2 \left(\frac{C.V.}{100} \right)^2 \right]^{\frac{1}{2}}$$

In this paper the approximate formula was used in all cases.

Besides the above mentioned constants, the probable error in per cent for the mean was also determined by dividing the probable error of the mean by the mean and multiplying by 100. This gives a better comparison of the errors, which in the case of plot 5A and 6A were 0.78 and 0.34 per cent, respectively.

According to Davenport (5, p. 438), the probable error is calculated for any number of variates fixes a range above and below the determined value such that the chances are even that the true value lies within this range. The chances are also even that this value lies outside of the limits set by the probable error, but by multiplying the probable errors of plot 5A and plot 6A by 3, we get 2.34 and 0.99 per cent, respectively, and the chances would be 21 to 1 that the true value would lie within the limits set by the probable errors.

EXPERIMENTAL DATA

The experimental data for the two plots are reported in tables 1 and 2, only the pounds per acre being tabulated, together with the ± pounds deviation from the mean.

It will be noted that the extreme range for the total nitrogen in plot 5A is from 1852 to 2966 pounds, and for plot 6A, 2216 to 2632 pounds, or a difference between the two extremes of 1114 and 416 pounds respectively. This is some indication as to the soil variability that is apt to be encountered in sampling soils.

If but a single sample had been taken to represent either of these plots, it can be readily seen that a very inaccurate estimation of the nitrogen content might have been made. The statistical constants calculated and tabulated at the ends of tables 1 and 2 represent the soil variability (4) in a mathematical way.

It will be noted that the probable error of the mean in plot 5A is 18.7 pounds of nitrogen, or over twice that of plot 6A, which is 8.0 pounds. The standard deviation and coefficient of variability for plot 5A are more than double that of plot 6A, showing the soil of plot 5A to be much more variable than that of plot 6A.

The probable errors as calculated in tables 1 and 2 include both the field and laboratory errors.

<center>LABORATORY ERROR</center>

To determine the laboratory error, twenty-four nitrogen determinations were made on a single sample of soil which was a composite made up by

<center>TABLE 1</center>
<center>*Nitrogen as determined for various samples on plot 5A*</center>

SAMPLE NUMBER	NITROGEN PER 2,000,000 POUNDS	DEVIATION FROM MEAN ±	SAMPLE NUMBER	NITROGEN PER 2,000,000 POUNDS	DEVIATION FROM MEAN ±
	lbs.	*lbs.*		*lbs.*	*lbs.*
1	2714	186	27	2574	46
2	2622	94	28	2472	56
3	2638	110	29	2508	20
4	2836	308	30	2682	154
5	2659	131	31	2628	100
6	2592	64	32	2697	169
7	2641	113	33	2461	67
8	2690	162	34	2416	112
9	2610	82	35	2377	151
10	2792	264	36	2475	53
11	2569	41	37	2283	245
12	2664	136	38	2450	78
13	2675	147	39	2591	63
14	2821	293	40	2453	75
15	2594	66	41	2221	307
16	2514	14	42	2430	98
17	2527	1	43	2312	216
18	2651	123	44	2471	57
19	2758	230	45	2398	130
20	2966	438	46	2346	182
21	2744	216	47	2206	322
22	2487	41	48	2320	208
23	2548	20	49	2158	370
24	2586	58	50	2271	252
25	2598	70	51	1852	676
26	2726	198	52	2196	322

$$\text{Mean (M)} = 2528 \quad \pm 18.7 \text{ lbs.}$$
$$\sigma = 199.5 \pm 13.2 \text{ lbs.}$$
$$\text{C. V.} = 7.88 \pm .52 \text{ per cent}$$
$$\text{P.E.}_m = 0.78 \text{ per cent}$$

using 10 gm. of soil from each of the fifty-two samples of plot 6A. The results of these determinations are given in table 3.

The extreme range for the twenty-four determinations was 2368 to 2422 pounds of nitrogen per acre, or a difference between the extremes of 54 pounds. The laboratory error for the twenty-four determinations was very low, being only ±1.6 pounds, or 0.07 per cent of the mean.

In sampling soil, it is often desirable to make a composite sample, thus eliminating a great deal of labor in making chemical analyses. This would be especially true when a large number of plots are to be sampled.

TABLE 2

Nitrogen as determined for various samples on plot 6A

SAMPLE NUMBER	NITROGEN PER 2,000,000 POUNDS	DEVIATION FROM MEAN ±	SAMPLE NUMBER	NITROGEN PER 2,000,000 POUNDS	DEVIATION FROM MEAN ±
	lbs.	lbs.		lbs.	lbs.
1	2360	33	27	2338	55
2	2296	3	28	2334	59
3	2276	116	29	2428	35
4	2352	41	30	2504	111
5	2308	85	31	2418	25
6	2292	101	32	2484	91
7	2282	111	33	2382	11
8	2346	47	34	2364	29
9	2252	141	35	2470	77
10	2298	95	36	2378	15
11	2368	25	37	2400	7
12	2394	1	38	2556	163
13	2218	175	39	2450	57
14	2294	99	40	2322	71
15	2426	33	41	2516	123
16	2374	19	42	2632	239
17	2418	25	43	2350	43
18	2356	37	44	2592	199
19	2216	177	45	2404	11
20	2448	55	46	2480	87
21	2338	55	47	2472	79
22	2364	29	48	2488	95
23	2426	33	49	2416	23
24	2442	49	50	2398	5
25	2362	31	51	2442	49
26	2468	75	52	2434	41

Mean (M) = 2393 ± 8.0 lbs.
σ = 85.7 ± 5.7 lbs.
C. V. = 3.58 ± 0.24 per cent
P.E.$_m$ = 0.34 per cent

Waynick and Sharp (10) have shown in their work that a composite sample is reliable after the soil variability is known. A like comparison was made by the author and the results are given in table 4.

The probable error in the difference is 8.2 pounds, while the difference between the two means is only 1 pound, or $\frac{1}{8}$ of the probable error in the difference, which, according to Reitz and Smith (5, p. 47) would be insignificant. That is, when the difference in two results is less than three times

the probable error in the difference, it is said to be due to random sampling, but as the difference in the two results increases to five or ten times the probable error, it is said to be significant.

From the data given in table 4, it would seem that the use of a composite sample would be justifiable after the soil variability has been determined.

TABLE 3

Nitrogen as determined on a uniform sample

SAMPLE NUMBER	NITROGEN PER 2,000,000 POUNDS	DEVIATION FROM MEAN ±	SAMPLE NUMBER	NITROGEN PER 2,000,000 POUNDS	DEVIATION FROM MEAN ±
	lbs.	*lbs.*		*lbs.*	*lbs.*
1	2382	10	13	2382	10
2	2404	12	14	2398	6
3	2422	30	15	2382	10
4	2392	0	16	2398	6
5	2394	2	17	2388	4
6	2400	8	18	2400	8
7	2382	10	19	2388	4
8	2386	6	20	2382	10
9	2374	18	21	2384	8
10	2398	6	22	2368	24
11	2398	6	23	2388	4
12	2412	20	24	2400	8

Mean (M) = 2392 ± 1.6 lbs.
σ = 11.8 ± 1.2 lbs.
C.V. = 0.48 ± 0.47 per cent
$P.E._m$ = 0.07 per cent

TABLE 4

A comparison of nitrogen determinations on a composite sample to those on individual samples

	MEAN POUNDS PER ACRE	PROBABLE ERROR ±
	lbs.	*lbs.*
Determinations on 52 individual samples (from table 2)...	2393	8.0
24 determinations on a composite of 52 samples Table 3)...	2392	1.6
Difference...	1	8.2*

* The probable error in the difference (5) being $\sqrt{(e_1)^2 + (e_2)^2}$ where e designates the probable errors of the two results compared.

NUMBER OF SAMPLES REQUIRED FOR ANY DEGREE OF ACCURACY

In sampling plots it is often desirable to know how many samples should be taken to be within the limits of a certain error. This may be determined mathematically from the results of tables 1 and 2 and tabulated as in table 5.

After the standard deviation is known for any given area, it is possible to vary the number of determinations in the formula

$$P.E._m = \frac{0.6745 \, \sigma}{\sqrt{n}}$$

and obtain the different probable errors given in table 5 and shown graphically in figure 2. Or, it is possible to start with a certain probable error and thus determine the number of samples necessary to be within the limits of the required error. For example, suppose we allowed an error of ±18.7

TABLE 5

The total probable error decreases as the number of samples increases

NUMBER OF SAMPLES	PLOT 6A		NUMBER OF SAMPLES	PLOT 5A	
	Probable error of mean ±			Probable error of mean ±	
	lbs.	per cent		lbs.	per cent
1	57.8	2.41	1	134.6	5.32
2	41.3	1.73	2	96.1	3.80
4	28.9	1.20	4	67.3	2.66
8	20.6	0.86	8	48.0	1.90
12	16.5	0.69	12	38.4	1.51
16	14.4	0.60	16	33.6	1.33
20	12.8	0.54	20	29.9	1.17
24	11.8	0.49	24	27.5	1.08
28	10.9	0.46	28	25.4	1.00
36	9.6	0.40	36	22.4	0.88
52	8.0	0.34	52	18.7	0.78

pounds of nitrogen and used the standard deviation from plot 5A, the formula would be

$$18.7 = \frac{0.6745 \times 199.5}{\sqrt{n}}.$$

Solving the equation would give fifty-two samples the number required to give an error of 18.7 pounds of nitrogen. In a like manner, the number of samples for any desired probable error could be calculated. It will be noted that to get a probable error of ±28.9 pounds in plot 6A, four samples should be taken. This will apply only to plots $\frac{1}{88}$ acre in size and quite uniform. In plot 5A four samples would give a probable error of ±67.3 pounds.

The laboratory error decreases or increases just as the total error, as shown in table 6.

The results of the twenty-four determinations made on a single sample in table 3 were used as a basis in calculating the probable laboratory errors, for the varying number of samples in the preceding table. The errors determined in table 6 are graphed in figure 2, and it will be noted that in most work this small error might well be disregarded.

DETERMINATION OF THE FIELD ERROR

In this type of work, there are two errors, namely, field error, which is due to soil variation and random sampling and the laboratory error obtained
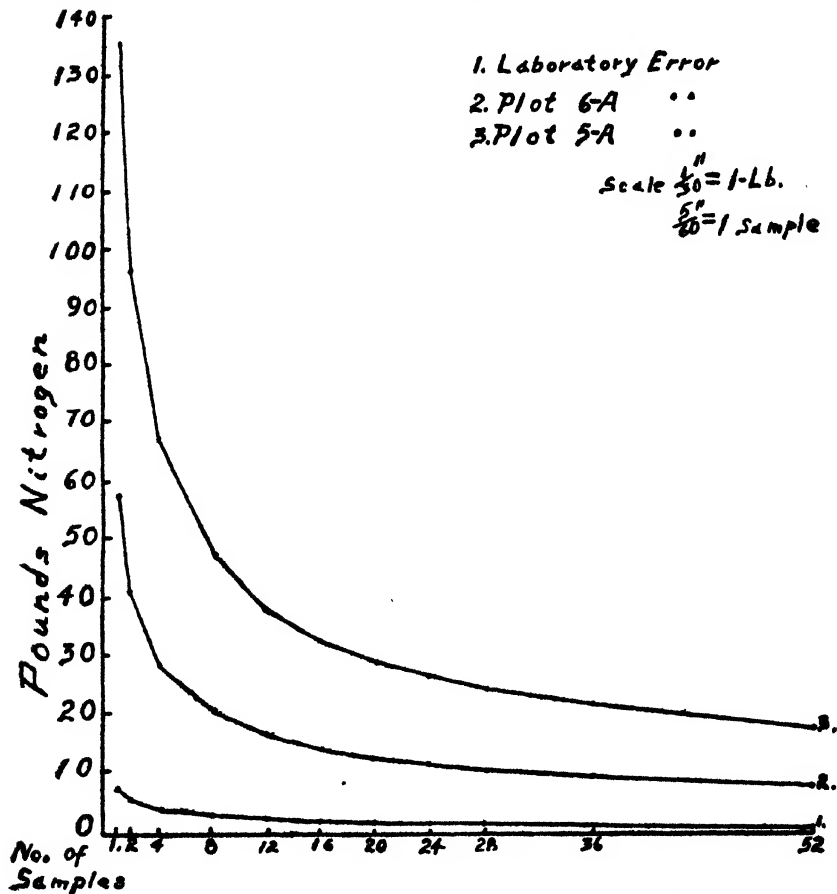
FIG. 2. PROBABLE ERRORS CALCULATED FOR VARYING NUMBERS OF SAMPLES

through manipulation. If we let E represent the total error of the mean with e_1 the laboratory error and e_2 the field error (7), we have

$$E = \sqrt{(e_1)^2 + (e_2)^2}$$

That is, the total error E is not the sum of the two errors as determined, but the square root of the sum of the squares of the separate errors.

In that the values E and e_1 have been determined in tables 1 and 6, the value e_2 can be calculated by substituting in the above formula, as

$$18.7 = \sqrt{(e_2)^2 + (1.1)^2} \text{ or } e_2 = \sqrt{(18.7)^2 - (1.1)^2} = \pm 18.6$$

It is worthy of note that by using the above formula, the field error is practically the same as the total error E, showing a reduction of only 0.1 pound of nitrogen.

TABLE 6

The laboratory error decreases as the number of determinations increases

NUMBER OF DETERMINA-TIONS	PROBABLE ERROR OF MEAN ±		NUMBER OF DETERMINA-TIONS	PROBABLE ERROR OF MEAN ±	
	lbs.	*per cent*		*lbs.*	*per cent*
1	7.96	· 0.33	20	1.77	0.07
2	5.68	0.24	24	1.62	0.07
4	3.99	0.17	28	1.50	0.06
8	2.84	0.12	36	1.32	0.06
12	2.27	0.09	52	1.10	. 0.05
16	1.99	0.08			

TABLE 7

Summary of the probable errors for plots 5A and 6A

PLOT NUMBER	NUMBER OF SAMPLES	E	e_1	$e_2 = \sqrt{(E)^2 - (e_1)^2}$	
		lbs.	*lbs.*	*lbs.*	*per cent*
5A	52	18.7	1.1	18.6	0.73
6A	52	8.0	1.1	7.9	0.33

TABLE 8

The soil variability by quarters for plots 5A and 6A

QUARTER NUMBER	FOUR SAMPLES AVERAGE NITROGEN PER QUARTER		QUARTER NUMBER	SIX SAMPLES AVERAGE NITROGEN PER QUARTER	
	Plot 5A	Plot 6A		Plot 5A	Plot 6A
	lbs.	*lbs.*		*lbs.*	*lbs*
1	2293	2424	1	2420	2417
2	2647	2314	2	2601	2356
3	2143	2459	3	2403	2485
4	2701	2314	4	2756	2321

Table 7 summarizes the probable errors for both plots, including the total error E, the laboratory error e_1 and the field error e_2. The values for E and e_1 necessary to calculate the per cent field errors were not tabulated in table 7. However, the same method was used as for pounds nitrogen. It will readi y be seen from the data in table 7 that plot 5A is much more variable than 6A as shown by the probable errors in columns 5 and 6 Another point

of interest in table 7 is the field error, e_2, which, in the case of plot 5 A is only 0.1 pound less than the total error, while the field error for plot 6 A is 0.1
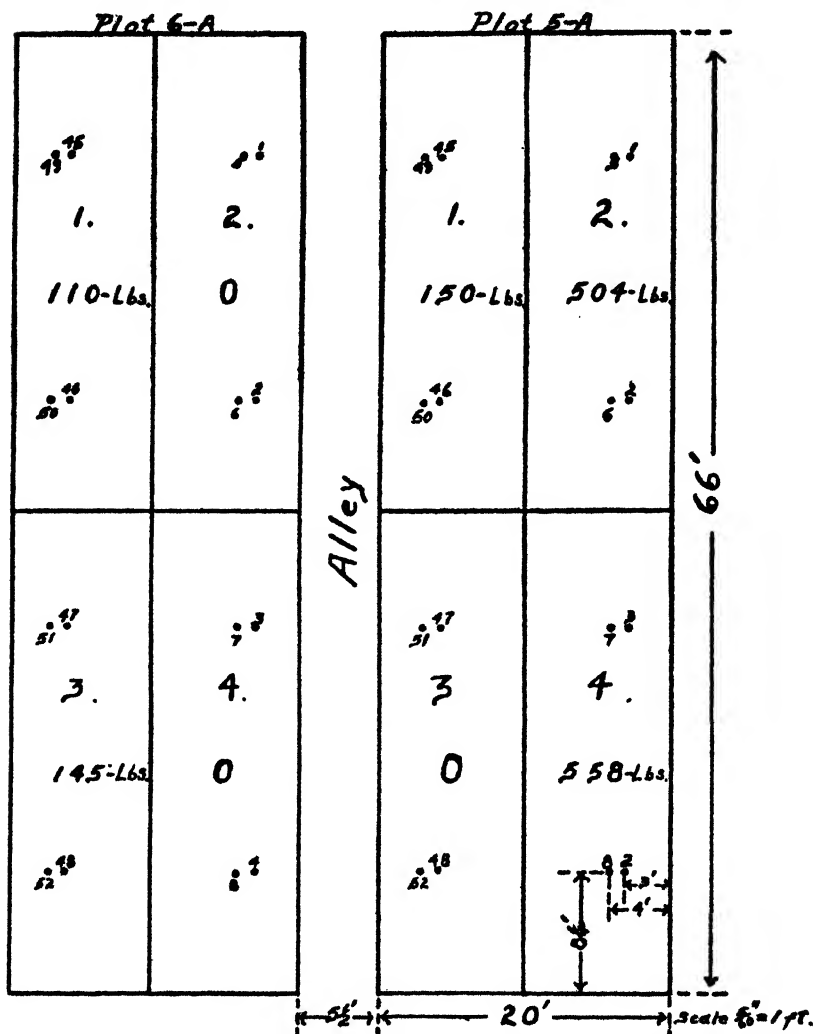
FIG. 3. SHOWING THE SOIL VARIABILITY WHEN FOUR DETERMINATIONS WERE AVERAGED FOR EACH QUARTER

pound less than the total error, showing that in most analytical work of this kind the laboratory error could be disregarded.

ACTUAL SOIL VARIABILITY IN POUNDS PER ACRE

By making a careful study of the two plots 5A and 6A, it was found that one-half of each plot was higher in nitrogen content than the other. This point was of most significance in the manured plot. Thus, to show the actual soil heterogeneity, the plots were divided into quarters and the nitrogen de-
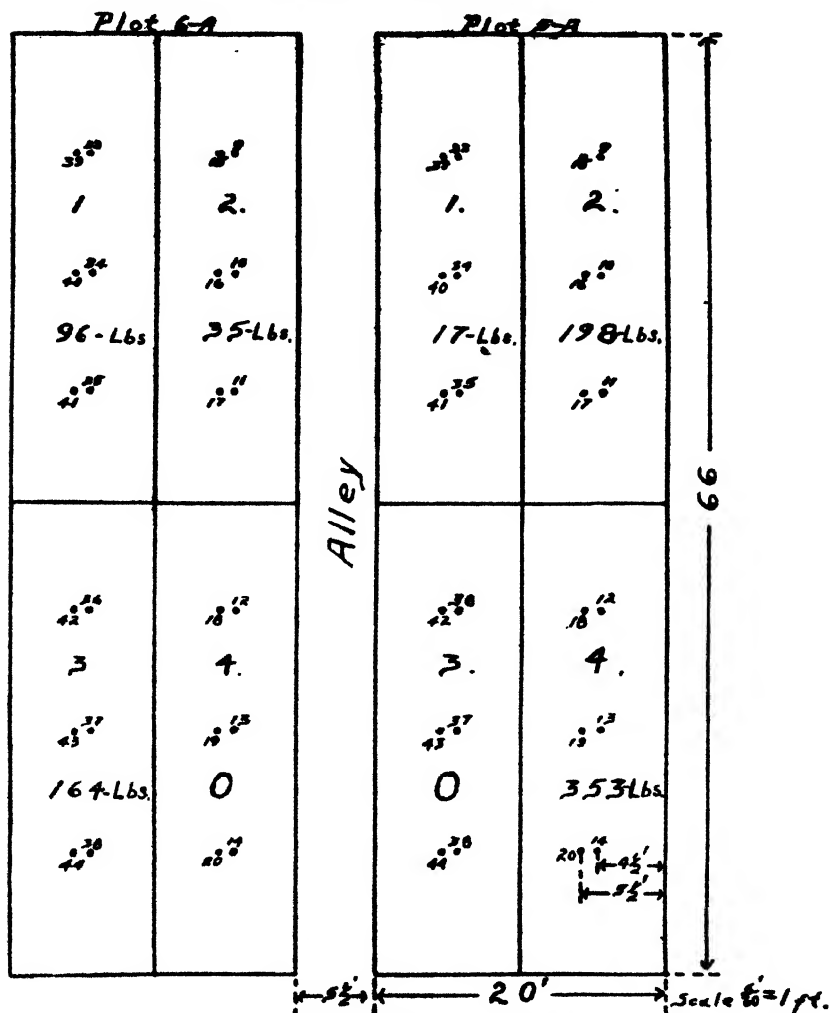
FIG. 4. SHOWING THE SOIL VARIABILITY WHEN SIX DETERMINATIONS WERE AVERAGED FOR EACH QUARTER

termined for each quarter by averaging four and six samples respectively. Table 8 gives the results obtained when the above-mentioned samples were averaged.

The results in the above table were figured on the acre basis. In comparing the quarters of each plot, the one having the lowest mean was taken as zero and subtracted from each of the remaining 3 quarters, giving them the values as shown in figures 3 and 4. The plots were drawn to scale and in the same order as they occurred in the field. Thus figures 3 and 4 show the arrangement of each plot and the pounds of nitrogen that each quarter varies from zero, or the lowest quarter.

In figure 3, where four samples were averaged, there was very little variation in the case of plot 6A, but considerable variation for plot 5A. It will be noted that the quarters next to the alley are lowest in both plots.

When six borings were averaged, as in figure 4, the variation was not so pronounced, but in about the same proportion, this reduction in the variation probably being due to the increased number of samples averaged and the fact that the borings in figure 3 were 3 feet from the alley, while in figure 4 they were 4½ feet from the alley. There was a slight depression between the two plots, and it is just possible that in plowing some of the lighter subsurface soil has been mixed with the richer surface soil, thus lowering the nitrogen content.

If the variability of these plots were not known, it is apparent that the taking of 1 or 2 borings would be of little value. Thus it seems necessary, when accuracy is demanded, to first take enough samples from any given plot to determine the variability of the soil. After this has been done, a composite sample consisting of a determined number of borings would probably give sufficiently accurate results for future analyses.

SUMMARY

The results obtained in this paper and the literature cited may be summarized as follows:

1. Soil plots that appear fairly uniform may show a large variation in nitrogen content among samples.

2 The application of manure to the soil increases the soil variability, the greatest variation or the manured plot 5A, being 1114 pounds of nitrogen, as compared to 416 pounds for the non-manured plot, 6A.

3. Due to soil variability, the statistical constants calculated for one area would not be comparable to any other. This is brought out forcibly by the results in this paper with the probable error of plot 5A being 0.78 per cent as compared to 0.34 per cent for plot 6A, the two plots being only 5½ feet apart.

4. The use of a single sample is of very little value for accuracy in experimental work.

5. A composite sample is of value only after the soil variability has been determined; then enough determinations shou'd be made on the composite to `nsure a va'ue representative of the soil mass.

6. With careful manipulation, the laboratory error is very low and might well be disregarded, thus making the field error practically the same as the total error.

7. After the soil variability has been determined for any plot, it is possible to calcu'ate the number of samples necessary to be within the limits of a certain error.

CONCLUSION

Thus it seems that to determine the field error in sampling any p!ot, a fairly large number of samples should be taken and statistical methods applied to the results. The field error determined in this way will be large or small according to the soil variability of the particular plot sampled.

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THE AVAILABLE STATE

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In ordinary cultivated soils the "total phosphoric acid" found by chemical analysis usually amounts to somewhere in the neighborhood of 0.1 per cent of the "air-dried fine earth." According to the conventional methods of computation this represents 2000–3000 pounds of that ingredient per acre; yet applications of 20 or 30 pounds of phosphoric acid in the form of super-phosphate may produce a large or even a manifold increase in the crops. This paradoxical result has not been satisfactorily explained. To say that the total phosphoric acid is not all available to the plants is merely to restate the problem since the available state can neither be measured nor defined.

It is commonly held that solution and ionization is a condition precedent to absorption of solids by plants and that the available state must be defined in terms of solubility. Dyer (1) thought that a 1 per cent solution of citric acid acting under arbitrarily defined conditions would serve as a critical re-agent to distinguish between that which is available and that which is not. He showed that the productive capacity of soils is more closely correlated with the amount of phosphoric acid soluble in this reagent than with the total phosphoric acid; and he suggested that soils which contain less than 0.01 per cent might be expected to respond to applications of phosphatic manure. This has been confirmed by innumerable observations by others, but prob-ably very few now regard the method as affording a reliable indication of the manurial requirements of soils. In any case it is and has long been recog-nised that the term "available" in this connection is an unfortunate mis-nomer, for it is barely conceivable that applications of 20 or 30 pounds of available phosphoric acid should produce the effects observed if ten times that amount were already present in the soil.

It is certain that the returns for manure diminish with each successive unit applied. It is no less certain that they diminish in some regular, definite order. If that order is known, or can be determined, the amount of available phosphoric acid originally present in the soil can be inferred from the incre-ment in the crops produced by applications of different amounts of unques-tionably available (water-soluble) phosphates.

Mitscherlich (4), working under controlled conditions, found that the increments produced by successive units of any essential constituent of the plants diminish in geometric progression.

$$\frac{dy}{dx} = K \ (M - y), \text{ or } y = M \ (1 - e^{-kx})$$

Thus, it might be stated that the increment produced by unit quantity of any constituent of which there is a deficiency is proportional to the difference from the maximum. K is a constant; y, the amount of crop corresponding to x units of the fertilizing ingredient, and M the maximum obtainable by addition of any amount of the same.

This thesis has been the subject of much controversy. It has been vigorously attacked (3) and stoutly defended (6). The criticism has developed chiefly along two lines; viz., that the thesis is not exact and that in any case it is not applicable under field conditions. In reply to the former, Mitscherlich points to his experimental results. These are convincing but it has been objected that the simple logarithmic curve corresponding to the formula is not the only one that can be drawn through the points determined. In particular it seems that the true curve may develop a certain reflex bend, resulting from a more or less marked lag in the rate of growth, towards the lower extremity.

To the second objection Mitscherlich rejoins, in effect, that any variation in the experimental conditions would alter the values of the constants K and M but would not otherwise affect the accuracy of the formula which expresses a fundamental law. If the thesis is exact it must apply to experiments in field plots as well as those in flower-pots; but the amount of produce is affected by so many conditions which cannot be controlled in the field that it may be impossible to discern the operation of the law.

The object of the present investigation is, assuming the fundamental truth of Mitscherlich's thesis, to find whether its operation can be traced in the records of field experiments and, if so, to determine from these data the amount of available phosphoric acid originally present in the soil.

The data first examined refer to the growth of lucerne in Australia (2). The experiment was begun in 1916 and the data are as follows:

	Cwt.	Cwt.	Cwt.
Superphosphate applied (1 cwt. = 112 pounds)	—	1	2
Average annual hay crop	15.25	28.75	37.25

It is fairly obvious that a curve, and only one consistent with the formula, can be drawn to pass through these three points; namely, that in which $M = 51.78$, $K = 0.4614$ and $x = 0.7556$. This value of x is the amount of superphosphate, in hundredweight, equivalent to the "available" phosphoric acid originally present in the soil, i.e., in the plot to which no manure was given. With the addition of 1 cwt. of superphosphate, the amount is increased to $(x + 1)$, with 2 cwt. it is increased to $(x + 2)$ and so on. The grade of manure used is not mentioned in the published account of the experiment, but assum-

ing that it was 30 per cent soluble, these values would correspond to 11.63 pounds, 27.02 pounds and 42.41 pounds of phosphoric acid per acre, respectively.

In figure 1 this curve has been drawn from the point of origin, i.e., from the point at which the amount of available phosphoric acid in the soil is zero. When the amount of manure added is zero, the amount of available phosphoric acid in the soil was, as shown above, 11.63 pounds per acre. The parts of the ordinates shown indicate the amounts of increase produced by each successive unit (cwt.) of manure added. A reflex bend in the curve like that of the broken line would not affect the inference regarding the amount of available phosphoric acid in the soil when no manure was given.
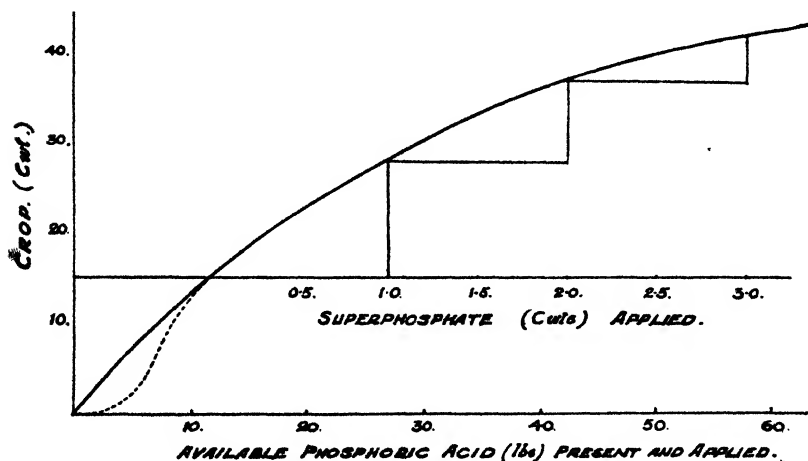
FIG. 1. CURVE SHOWS THE AMOUNT OF CROP CORRESPONDING TO THE QUANTITY OF AVAILABLE P₂ O₅ IN THE SOIL AND THE INCREASE PRODUCED BY EACH UNIT OF FERTILIZER APPLIED

The hay was valued at £3 10/- per ton and the superphosphate cost 7/- per cwt. The quantity of the latter might therefore have been increased advantageously to about 5 cwt. This represents nearly 77 pounds of phosphoric acid in addition to the 11.63 pounds present originally, and would have increased the crop to 48 cwt. of hay per acre. In the author's opinion the cost of spreading should have been added to the price of the manure and the cost of harvesting should have been deducted from the value of the crop. If that were done it would not be profitable to use more than about 4 cwt. of superphosphate. But taking the figures as they stand it appears that under similar conditions of climate and soil it would not be necessary or advantageous to apply phosphatic manures to lucerne on soils that contain more than about 85 pounds per acre of phosphoric acid actually available to the plants.

If the conclusions drawn are exact the effects of the manure are readily intelligible. In the circumstances considered a ton of lucerne hay would be produced if the soil contained 15.5 pounds of available phosphoric acid. By the application of 1 cwt. of superphosphate the amount of available phosphoric acid in the soil is doubled, by the application of 2 cwt. it is trebled and so on. The crops would not, of course, be increased in the same ratio but, if they were not limited by deficiency in other conditions, large increments would naturally be expected from such manifold increments in the amount of available phosphoric acid.

These considerations also help to establish a connection between the chemical composition of crops and their manurial requirements. The apparent absence of such connection at present is generally felt to be disturbing. A root crop removes from the soil about twice as much phosphoric acid as a hay crop, i.e., the amount required for an average crop of the latter would only suffice for about half a crop of the former. If this amount of available phosphoric acid were doubled by applying superphosphate the root crop would be increased by about 100 per cent but the hay crop would only be increased by (say) 10 per cent. At all events, with any given amount of available phosphoric acid short of the maximum in the soil, root crops would respond better than hay crops to applications of phosphatic manure. It is not necessary to assume that the grasses have a greater assimilative capacity than the roots. It is of course, quite possible that such is the case but the difference, if any, is perhaps not so great as has hitherto been generally supposed. The failure of chemical analysis to distinguish with certainty between soils which require phosphatic manure and those which do not is also accounted for. Suppose a soil to contain 275 pounds per acre of phosphoric acid soluble in dilute citric acid, that of this amount 25 pounds were actually available and that an additional 50 pounds—say 4 cwt. of superphosphate—were applied; the amount of citric soluble phosphoric acid would be only 0.011 per cent in the former case and 0.013 per cent in the latter. Such a small difference would generally be regarded as negligible though it would actually mean a threefold increase in the amount of available phosphoric acid. In short, chemical analysis has failed because, generally, the percentages of total phosphoric acid, citric soluble phosphoric acid, available phosphoric acid in productive soils and available phosphoric acid in unproductive soils are respectively of the order of 10^{-1}, 10^{-2}, 10^{-3} and 10^{-4}.

Additional evidence in support of these important inferences has been obtained from the records of an experiment carried out by the author in the years 1893–1896 inclusive. The objects of this experiment were to determine the maximum amount of phosphatic manure that could be profitably applied, with and without nitrogen, to hay crops on a flat alluvial meadow at Falcondale in Cardiganshire, and to compare superphosphate with basic slag as a source of phosphate, and nitrate of soda with sulfate of ammonia as a source of nitrogen. The quantities of manure were adjusted to represent

TABLE 1

Weight (cwt.) of hay from each plot, the maximum (M), constant (K) and amount of available phosphates (X) originally present in the soil

	EXPERIMENTAL DATA				INFERENTIAL DATA		
Treatment	Superphosphate				*M*	*K*	*x*
	A. None	B. 1 cwt.	C. 2 cwt.	D. 3 cwt.			
	cwt.	*cwt.*	*cwt.*	*cwt.*			
1893							
I. No nitrogen...............	4.86	5.93	6.63	⎧ *7.11** ⎨ 7.14 ⎩ *11.84*	8.00	0.417	2.264
II. 112 pounds NaNO₃..........	10.00	11.57	11.79	⎰12.21	11.85	1.888	0.984
III. 224 pounds NaNO₃..........	13.50	18.43	18.58	18.58			
IV. 90 lbs. (NH₄)₂SO₄...........	7.97	10.58	10.58	8.71			
V. 180 pounds (NH₄)₂SO₄.......	10.92	12.06	12.93	⎰*13.21* ⎱15.00	15.55	0.238	4.285
1894							
I. No nitrogen...............	21.72	⎰*26.31* ⎱18.07	27.72	28.15	28.36	1.176	1.235
II. 112 pounds NaNO₃..........	24.43	30.36	34.00	⎰*36.21* ⎱35.00	39.74	0.490	1.946
III. 224 pounds NaNO₃..........	⎰*29.42* ⎱25.28	37.71	40.86	42.14	42.79	0.968	1.202
IV. 90 pounds (NH₄)₂SO₄.......	25.43	31.15	32.36	⎰*32.66* ⎱31.72	32.74	1.526	0.983
V. 180 pounds (NH₄)₂SO₄.......	34.15	38.00	39.14	⎰*39.38* ⎱39.43	39.49	1.276	1.568
1895							
I. No nitrogen...............	8.84	11.71	⎰*13.81* ⎱15.86	15.29	19.36	0.318	1.929
II. 112 pounds NaNO₃..........	10.15	15.86	18.28	⎰*19.31* ⎱17.43	20.05	0.860	0.821
III. 224 pounds NaNO₃..........	14.00	16.71	⎰*18.18* ⎱21.57	19.00	20.00	0.601	2.004
IV. 90 pounds (NH₄)₂SO₄.......	11.14	13.00	14.42	⎰*15.52* ⎱12.57	19.09	0.267	3.286
V. 180 pounds (NH₄)₂SO₄.......	14.57	15.71	⎰*16.10* ⎱13.28	16.14	16.29	1.087	2.068
1896							
I. No nitrogen...............	14.63	17.93	19.93	⎰*21.13* ⎱22.64	23.00	0.501	2.017
II. 112 pounds NaNO₃..........	18.58	21.64	⎰*23.98* ⎨26.07 ⎩*29.45*	25.78	31.81	0.263	3.332
III. 224 pounds NaNO₃..........	24.72	27.79	27.79	30.36	31.42	0.613	2.522
IV. 90 pounds (NH₄)₂SO₄.......	20.35	22.51	23.29	⎰*23.49* ⎱19.22	23.62	1.081	1.830
V. 180 pounds (NH₄)₂SO₄.......	29.85	27.94	23.08	26.94			

* The figures in italics are the amounts of crop calculated by the formula for the plots not involved in the determination of M, K and X.

equal amounts of phosphoric acid and equal amounts of nitrogen from the sources of these ingredients, respectively.   The plan of the experiment, as far as the superphosphate is concerned, will be sufficiently obvious from table 1.

It will be seen that there was a control plot and three others to which different quantities of superphosphate were applied in each case.   This gives altogether four points on each curve and the values of M, K and x can be determined from any three of them, i.e., in four different ways.   If the data were absolutely (mathematically) consistent precisely the same results would, of course, be obtained in each case.   Such perfection is not, however, attainable in matters of this kind and the choice of alternatives was at first embarrassing.   It is obvious, however, that the values obtained from the first three plots (A, B, and C) are generally to be preferred because in many cases the increase produced by the third hundredweight of superphosphate (plot D) brings the crop very near to the attainable maximum and any variations due to experimental error and uncontrolled causes affect the values (M, K and x) to a much greater extent than when these are calculated from data in which the margin is wider.

Irregularities arising from these causes are not, of course confined to plot D but presumably affect the crops on all the plots in greater or less degree.   In some cases they are easily detected.   For example when the produce from one of the manured plots is less than that of the control the result is clearly a discrepancy.   Or, again, if the amounts of increase produced by successive units of manure applied are not in the order of diminishing quantity the data must be regarded as untrustworthy; and, in such cases, it is often easy to decide which plot is out of order.   Altogether, three plots, viz., plots III and IV in 1893, and plot V in 1896 had to be discarded for these reasons; the irregularities being such that no inference could be drawn.   In all the other cases the values of M, K, and x were determined from the three plots that seemed most consistent, and the amount of the crop calculated by the formula for the fourth plot, which was not involved in the determination of M, K and x, is shown in italics above the result actually obtained.

The irregularities are naturally greater and of more frequent occurrence in abnormal seasons.   Unfortunately, only in one year, 1894, out of the four could the season be described as normal.   In that year, 21 cwt. of hay was obtained from the control plot and nearly twice as much from some of those to which manures were applied.   The first year of the experiment, 1893, was characterized by prolonged drought and only about a quarter crop was produced.   In 1895 and 1896 the drought was not so severe and in these two seasons the crops amounted to about half and three-quarters of the normal yield, respectively.

Keeping these facts in mind the figures in the table may be left to tell their own tale.   The two points to which attention should be more particularly directed are (a) comparison of the observed results (in ordinary type) with those calculated (in italics above) and (b) the value of x which is the amount

of superphosphate equivalent to the available phosphoric acid originally present in the soil. To determine the latter, it has been said, is the principal object of the investigation; the former is of impotance only as a test of the reliability of the estimate. To facilitate comparison the condensed results are presented in table 2.

The uniformity of the figures in the last column is, in the circumstances, quite remarkable. It signifies, apparently, that the amount of available phosphoric acid, as determined by this method, is not affected by the presence or absence of nitrogenous manures or by the kind or quantity of the same if used. The figures in the bottom row are not uniform; on the contrary, if the results for 1893 be ignored, they exhibit a progressive increase from year to year which probably represents the unexhausted residue of the manure applied in the preceding years. If this explanation be accepted and allowance made for it, the approximate uniformity thus inferred may be held to signify that the amount of available phosphoric acid as determined by this method, is not affected by drought or moisture except in so far as drought tends to produce irregularities which obscure the result.

TABLE 2

Available phosphoric acid in terms of superphosphate originally present in the soil (i.e., x)

↓	1893	1894	1895	1896	MEAN
	cwt.	*cwt.*	*cwt.*	*cwt.*	*cwt.*
No nitrogen................................	2.246	1.235	1.929	2.917	1.857
112 pounds NaNO₃.........................	0.984	1.946	0.821	3.332	1.771
224 pounds NaNO₃.........................		1.202	2.004	2.522	1.909
90 pounds (NH₄)₂SO₄......................		0.983	3.286	1.830	1.700
180 pounds (NH₄)₂SO₄.....................	4.285	1.568	2.068		2.604
Mean....................................	2.505	1.387	2.022	2.425	1.968

The mean of all the results is 2.015 ± 0.6 and in view of the magnitude of the probable error perhaps no great confidence can be reposed in the conclusions. It may be held that the figures represent no more than the irregularities due to the exceptional character of the seasons and that they have fortuitously combined to produce precisely the results to be expected. It is to be observed, however, that the season of 1894 was a normal one and that the results obtained in that year exhibit a satisfactory degree of consistency. Arguments founded on the mean for that year alone may therefore bear more stress than those above referred to.

At all events, notwithstanding the variations in detail, the important fact remains that the results are all essentially of the same order. They afford fairly conclusive evidence that the amount of available phosphoric acid originally present in this soil is equal to that contained in 1–2 cwt. of superphosphate (25 per cent soluble), i.e., in round numbers, about 20 pounds of phosphoric acid per acre, or about twice as much as was found in the case

of the more responsive Australian soil. By application of 1, 2, and 3 cwt. of superphosphate this would be increased to 33 pounds, 46 pounds, and 59 pounds, respectively. The last mentioned quantity, it will be seen, represents a threefold increase in the amount of available phosphoric acid.

A law of diminishing returns implies that the smaller the amount of any available plant food in the soil the larger will be the percentage of it removed by the crops, but that under no circumstances will the whole of it be utilized. The crop of 22 cwt. of hay obtained from the unmanured plot in 1894 would remove only 8 or 9 pounds of phosphoric acid out of the 20 pounds available. The crop of 5 cwt. obtained in 1893 would remove only about 2 pounds, i.e., about one-tenth of the amount available. It is remarkable that, in these circumstances, the crop in 1893 should have been increased by nearly 20 per cent by the application of 1 cwt. of superphosphate. This quantity of manure, itself, contained 13 pounds of available (water soluble) phosphoric acid, i.e., over six times as much as was removed by the crop, but a further increase was produced by the second hundredweight and a still further increase by the third. It is necessary, therefore, to inquire precisely what meaning is to be attached to the term available in this connection.

If it be true that solution and ionization is a condition precedent to absorption of salts by plants, only that portion of the phosphoric acid which is actually dissolved can be regarded as in any real sense available. In natural soils the amount of phosphoric acid in solution at any given time is relatively small. The average amount found by Voelcker (8) in the drainage water from Broadbalk field at Rothamsted was 0.93 parts per million. Reckoning the quantity of water in the soil as a fourth of the dry weight, this would represent only about 0.2 pound per acre. Whitney and Cameron (9) found from five to eight times as much in the soil solutions which they obtained by centrifugal methods. By the same method of computation this represents only from 1 to 1.5 pound of phosphoric acid in solution per acre. The film-water solution which cannot be extracted by this means is probably still more concentrated but there is no good reason to suppose that at any given time the amount of phosphoric acid in solution is as much as is removed in the crops during their period of growth.

But even if such were the case that quantity would not suffice for the requirements of the plants. The rate of diffusion would be reduced as the ions were withdrawn from the solution and infinite time would be required to complete the process. It is evident, therefore, that there must be a reserve of undissolved material able to pass more or less rapidly into solution and replenish the supply of ions. The rate at which this occurs will depend upon (a) the temperature and concentration of the existing solution, (b) the amount of carbon dioxide in the solution and therefore to some extent upon the amount of organic matter in the soil and the freedom of access of air to the same, (c) the state of combination in which the phosphoric acid is present and (d) upon the extent of surface exposed. Under like conditions in other

respects the rate at which ions removed by growing plants are replaced will be governed by the last mentioned condition.

The extent of surface varies inversely as the size (diameter) of the particles. The curve (fig. 2) by which this relationship is expressed is "L" shaped, i.e., it changes somewhat abruptly from the approximately horizontal to the approximately vertical direction as it approaches the zero point. The region of the bend probably corresponds to a critical stage similar to, if not identical with, that which marks the transition to the colloid state. It may be supposed, therefore, that the corner is turned by a range of particles of the order of 10^{-4} mm. in diameter and that any increase in the number of particles of smaller size will greatly accelerate the rate at which ions removed from the solution are replaced therein.
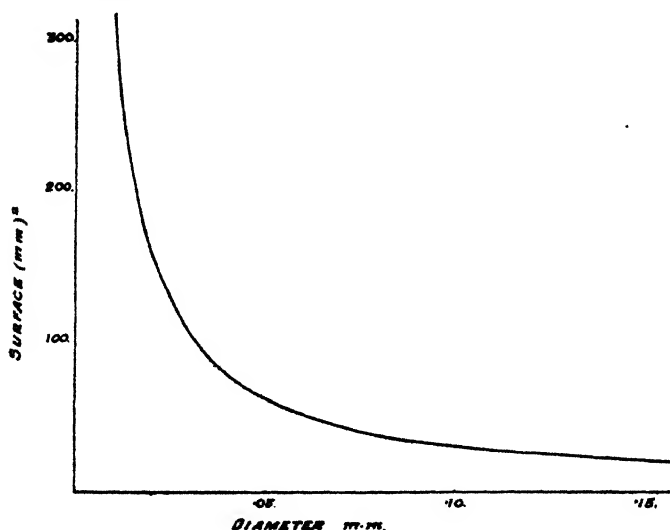
FIG. 2. THE CURVE ILLUSTRATFS THE INCREASE IN TOTAL SURFACE DUE TO FINE SUBDIVISION OF PARTICLES. THE REGION OF THE BEND PROBABLY CORRESPONDS TO A CRITICAL STAGE BETWEEN THE AVAILABLE AND NON-AVAILABLE STATES

When superphosphate is applied to soils the soluble phosphoric acid does not remain in that state but is converted into other compounds and solid particles are formed. It is not necessary to suppose that these particles are all of the same kind, or all of the same size, but only that a larger or smaller proportion of them are below the critical stage and therefore subject to comparatively rapid solution. When the number of particles of this degree of fineness becomes so large that the ions can be replaced as rapidly as they are removed any further increase would not affect the amount of the crop.

It has been shown that the soil now under investigation contains about 20 pounds per acre of available phosphoric acid and it is clear, from the method employed, that this means merely that the conditions prevailing in the soil are precisely those which would result from the application of superphosphate containing that amount of soluble phosphoric acid if none of that ingredient were originally present.

The results obtained, especially in 1893, cannot be explained on the assumption that the P_2O_5 applied as superphosphate remains soluble or in any real sense available to the plant; and to call that originally present in the soil available is to confuse the issue. The point to be emphasized is that it is essentially of the same character as that derived from superphosphate after it has reacted with the soil constituents. The term "superfine" appears aptly to describe this condition. This superfine phosphoric acid should not be confused with that which is soluble in 1 per cent citric acid. The term is to be understood as referring exclusively to the phosphoric acid which was earlier in this article described as actually available to plants. At that stage of the investigation it was considered right so to describe it because it was obviously as much available to plants as the water-soluble phosphate in the superphosphate applied.

The 20 pounds or so of superfine phosphoric acid per acre found in the soil is more than would be removed from the land by the heaviest crop obtained in 1924. It is ten times as much as would be removed by the crops of 1893; but evidently it was not enough to provide for replacement of the ions as quickly as they were removed from the soil solution in either case. It appears therefore that neither moisture nor nitrogenous manures accelerate the rate at which ions are abstracted to any considerable extent but merely prolong the period during which the process of abstraction continues. Such, at all events, is the hypothesis offered to account for the phenomena observed.

An attempt was made to determine the amount of "available" nitrogen in the same way but on examination the data were found to be too limited and irregular to afford any trustworthy results. Since then, however, Prescott (7) has published an account of experiments on the application of nitrate of soda and sulfate of ammonia to maize crops in Egypt in which the plots were more numerous and very consistent results were obtained. These, together with the inferential data, are reproduced below. As before, the figures in italics are the amounts of crop calculated for the plots not involved in the determination of M, K and x.

		KILOGRAMS PER ACRE				
Nitrate of soda................	....	100	150	200	300	400
Nitrogen in same..............	....	15.1	22.7	30.3	45.4	60.5
Crop (dry ears)...............	1610	2276	*2410* / *2524*	2730	*2936* / *3042*	*2910* / *3253*

$$M = 3708; K = 0.382; \frac{x}{100} = 1.49$$

		KILOGRAMS PER ACRE				
Sulfate of ammonia.............	....	75	150	200	250	300
Nitrogen in same..............	....	15.3	30.7	40.9	51.1	61.3
Crop (dry ears)...............	1610	2304	2670	2950	2930	3050
				2810	2902	2936

$$M = 3075; K = 0.6421; \frac{x}{100} = 1.155$$

For convenience in calculation, x was found in terms of hundreds of kilograms. The amount of "available" nitrogen originally present in the soil was therefore equivalent to:

149   kgm. nitrate of soda   = 22.5 kgm. nitrogen per acre
115.5 kgm. sulfate of ammonia = 23.6 kgm. nitrogen per acre

The large number of plots (6 in each case), the consistency of the data and the close agreement of the results obtained with two different kinds of manure tend to inspire confidence not only in this particular experiment but also in the method of investigation when subject to controlled conditions.

The 50 pounds of nitrogen per acre found to be originally present is not the total nitrogen in the soil. It is the amount of nitrogen potent in fertilizing effects as that in equivalent quantity of nitrate of soda or sulfate of ammonia. These substances are soluble in water and the nitrogen they contain is not converted into insoluble compounds by reaction with other soil constituents. It is reasonable to suppose therefore that this quantity (50 pounds per acre) of nitrogen was present in the form of soluble compounds and was truly available to the plants. As the yield of straw is not mentioned it is impossible to estimate exactly how much nitrogen was removed from each plot, but the amount was probably not far short of the total originally present and added in the manure.

In England the conditions are, of course, very different. So far as can be ascertained from the data previously given in the table the amount of "available" nitrogen originally present in the soil was only about 15 pounds per acre. Judging by the amount of nitrogen found in the drainage water at Rothamsted this is three or four times as much as would be present in the soil solution at any one time. In any case it is less than a third of the amount removed in the crop in 1894 from plot I D which received no nitrogenous manure. This implies the conversion of a large amount of nitrogen from an insoluble to a soluble state during the period of growth and is therefore in agreement with prevailing ideas on the subject. As the rate at which these changes occur depends so largely upon temperature and moisture the amount of available nitrogen present at any one time must be regarded as more or less

fortuitous. It does not appear therefore that this method of investigation is likely to prove of much value in regard to nitrogen as far as this climate is concerned.

The close correspondence of the results obtained under carefully controlled conditions, however, encourages the hope that it may be found possible to employ the method in the laboratory to determine the manurial requirements of soils as regards the mineral elements. The result of such experiments, if found to agree substantially with those of field trials, would furnish a valuable standard of comparison for any purely chemical methods which may be evolved in the future. It is to be expected that if the aim is once clearly established, suitable chemical methods will be discovered. It is already clear that such methods must be applied to samples of the soil taken *in situ*. To dry the soil, disintegrate it and eliminate the larger particles, euphemistically described as stones, is indefensible. Results expressed as percentages of the "air-dried fine earth" are useless.

SUMMARY

It is suggested that the amount of available phosphoric acid in soils may be found from the rate at which the amounts of increase produced by application of different quantities of water soluble phosphates diminish.

The amount so found in an Australian soil was about 11 pounds per acre and it is claimed that this explains the effect of the manure, accounts for the difference in the response of grass and root crops and for the failure of chemical analysis to determine with certainty the manurial requirements of soils.

In an English meadow soil the amount of available phosphoric acid found was, on the average of four years trial, about 20 pounds per acre. Much the same results were obtained in dry and wet seasons and they were not affected to any considerable extent by the applications of nitrogenous manures. In the third and fourth year the data bear evidence of the residual effects of the manure applied in the preceding years.

It is pointed out that water soluble phosphates revert to insoluble forms by reaction with other soil constituents, that the rate at which they are redissolved must depend largely on the size of the solid particles formed and that there must be a critical stage.

It is considered that only the phosphoric acid in solution is actually available to plants and that the amount of phosphates found by this method would be more accurately described as superfine phosphates because it is as potent as that applied in the form of superphosphate and must be presumed to be in an equally fine state of division.

The hypothesis offered to account for the phenomena observed is that ions are removed from the soil solution by growing plants and are replaced by the passing into solution of the most minute solid particles. The effect of the manure is to increase the number of these particles. When they are

so numerous that the ions are replaced as rapidly as they are abstracted the maximum effect of the ingredient applied is produced and the crop will not be further increased by addition of any larger quantity.

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INFLUENCE OF ORGANIC MATTER UPON THE DEVELOPMENT OF FUNGI, ACTINOMYCETES AND BACTERIA IN THE SOIL[1]

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It is a matter of common knowledge that the addition of organic matter to the soil greatly increases the development of microörganisms. It has also been recorded that the nature of the organic matter added influences not only the number of microörganisms but also the types developing in the soil.

We need cite only a few investigations on this subject. Engberding (4) found that the addition of 2 per cent of cane sugar to a soil brought about an increase of 1000 to 1500 per cent in the number of bacteria developing upon Heyden agar; addition of 0.5 per cent of dextrose brought about an increase of only 300–400 per cent. This increase was soon followed by a decrease and in some cases there were no more bacteria in the treated than in the control soils after two and one-half months. The addition of straw and green manure to the soil also increased the numbers of bacteria 300–600 per cent over the control. Stable manure and urine were also found to favor greatly the development of bacteria.

According to Bazarevski (1), the addition of dextrose to the soil increases the number of bacteria but diminishes the number of fungi, both in the presence and absence of available nitrogen salts. It was suggested that this may be due to the formation of a dry pellicle of sugar on the surface of soil preventing the admission of oxygen. Cellulose, however, greatly favored the development of fungi causing increases of 200–1000 per cent, and also favorably influenced the development of bacteria, especially in the presence of ammonium salts. Hiltner and Störmer (5), Conn (2) and others pointed out the fact that the addition of plant material increases the development of actinomycetes. Conn (3) found that fresh manure affects the development of the non-spore forming bacteria, but not of the spore formers.

The following data were obtained from studies concerned with the course of decomposition, in the soil, of organic substances of varying carbon-nitrogen ratio. The common plate method was used for the determination of the numbers. Bacteria and actinomycetes were determined on albumin agar (7). A special acid medium, described elsewhere (6), was used for the determination of fungi. Dextrose (0.5 per cent), cellulose (1 per cent filter paper) with and without soluble nitrogen (0.1 per cent $NaNO_3$), rye straw (1 per cent), alfalfa meal (1 per cent) and dried blood (1 per cent) were used as sources of organic matter. Thus a series of organic substances of varying nitrogen content were used; viz., dextrose and cellulose (free from nitrogen), straw (0.7 per cent nitrogen), alfalfa meal (2.5 per cent nitrogen), and dried blood (9.5 per cent nitrogen). The numbers of microörganisms in the soil

developing as a result of the addition of organic matter were determined ten
to seventeen days after the addition of the organic matter, except in the case

TABLE 1

Treatment of soils used in the experiments

SOIL NUMBER	ANNUAL TREATMENT	pH	FERTILITY	NITRATE-N IN 100 GM. OF SOIL INCUBATED FOR 20 DAYS
				mgm.
5A	Manure, minerals*	5.5	Very fertile	1.80
5B	Manure, lime, minerals*	6.7	Very fertile	1.55
7A	Untreated	5.1	Very poor	0.59
7B	Lime alone	6.5	Fair	0.66
9A	NaNO₃, minerals	5.8	Good	1.05
11B	(NH₄)₂SO₄, minerals, lime	6.0	Good	1.01

* Minerals = potassium salt and phosphate.

TABLE 2

Influence of 0.5 per cent dextrose upon the development of microörganisms in the soil after 2 days

SOIL NUMBER	FUNGI		BACTERIA + ACTINOMYCETES		ACTINOMYCETES	
	Start	End	Start	End	Start	End
			thousands	*thousands*	*thousands*	*thousands*
5A	87,300	109,400	6,500	43,000	1,800	3,000
5B	19,700	24,000	9,360	103,000	3,360	.....
7A	115,700	82,000	3,860	22,200	1,260	1,940
7B	20,000	25,400	7,760	22,000	2,760	.....
9A	73,300	102,000	8,000	47,400	1,500	1,740
11B	25,700	36,000	8,400	30,880	2,700	2,880

TABLE 3

Influence of 1 per cent cellulose, with and without NaNO₃, upon the development of microörganisms in the soil after 17 days

SOIL NUMBER	NaNO₃	FUNGI		BACTERIA + ACTINOMYCETES		ACTINOMYCETES	
	per cent	Start	End	*thousands*	*thousands*	*thousands*	*thousands*
5A	0	87,300	320,000	6,500	21,400	1,800	6,400
5A	0.1	87,300	3,100,000	6,500	40,600	1,800	4,600
7A	0	115,700	160,000	3,860	3,600	1,260	600
7A	0.1	115,700	4,800,000	3,860	4,800	1,260	400
7B	0	20,000	47,000	7,760	17,400	2,760	2,200
7B	0.1	20,000	290,000	7,760	47,200	2,760	3,200

of dextrose when a 48-hour period of incubation was used. The soil was kept
at optimum moisture content at 25–28°C. It was desirable to use short

periods of incubation since the most active decomposition and the greatest changes in the numbers and types of microörganisms occur shortly after adding the organic materials.

The soil used was a sassafras gravelly loam from a series of plots, whose fertility, physical, chemical and biological conditions have been modified as

TABLE 4

Influence of rye straw (1 per cent) upon the development of microörganisms in the soil after 10 days

SOIL NUMBER	FUNGI		BACTERIA + ACTINOMYCETES		ACTINOMYCETES	
	Start	End	Start	End	Start	End
			thousands	*thousands*	*thousands*	*thousands*
5A	87, 300	750, 000	6, 500	21, 800	1, 800	2, 800
5B	19, 700	24, 000	9, 360	29, 900	3, 360	2, 800
7A	115, 700	600, 000	3, 860	25, 200	1, 260	200
7B	20, 000	19, 000	7, 760	24, 400	2, 760	1, 900
9A	73, 300	650, 000	8, 000	23, 000	1, 500	1, 800
11B	25, 700	47, 000	8, 400	26, 000	2, 700	1,.800

TABLE 5

Influence of rye straw (0.5 per cent) and alfalfa meal (0.5 per cent), with and without $NaNO_3$ upon the development of microörganisms in the soil after 14 days

TREATMENT OF SOIL	FUNGI	BACTERIA + ACTINOMYCETES
Untreated...	38, 700	8, 875, 000
Straw..	136, 000	34, 200, 000
Straw + 0.025 per cent NaNO₃.....................	233, 000	35, 700, 000
Alfalfa..	297, 000	74, 600, 000
Alfalfa + 0.025 per cent NaNO₃...................	247, 000	73, 400, 000

TABLE 6

Influence of dried blood (1 per cent) upon the numbers of microörganisms in the soil after 12 days

SOIL NUMBER	FUNGI		BACTERIA + ACTINOMYCETES		ACTINOMYCETES	
	Start	End	Start	End	Start	End
			thousands	*thousands*	*thousands*	*thousands*
5A	87, 300	2, 079, 950	6, 500	381, 600	1, 800	190, 900
5B	19, 700	73, 300	9, 360	373, 000	3, 360	6, 000
7A	115, 700	1, 438, 300	3, 860	473, 900	1, 260	2, 200
7B	20, 000	125, 000	7, 760	352, 700	2, 760	500
9A	73, 300	1, 871, 650	8, 000	312, 200	1, 500	128, 700
11B	25, 700	311, 600	8, 400	107, 900	2, 700	42, 700

a result of fertilizer treatments for the last fifteen years. Table 1 indicates the treatments and present conditions of these soils.

The results given in tables 2–6 indicate the effects of various organic substances upon the development of microörganisms in these soils.

These studies confirmed the previous observations of Engberding, Bazarevski and others that dextrose increases primarily the development of bacteria, but not of fungi and actinomycetes.   This is due to several factors:

1. The majority of bacteria use dextrose in preference to higher carbohydrates and their derivatives, while many fungi readily decompose celluloses, pentoses, and other complex carbohydrates.

2. Bacteria generally require much less nitrogen for the synthesis of their cells per unit of dextrose decomposed than do the fungi, the latter producing an abundant mycelium, for which considerable nitrogen is required.

3. Among the bacteria, the nitrogen-fixing forms readily utilize dextrose as a source of energy without requiring any combined nitrogen.   Bacteria develop rapidly following the addition of dextrose, in the presence of even a small amount of available nitrogen while the fungi, which require a large amount of available nitrogen, or the actinomycetes, which develop only very slowly, may not be affected to any appreciable extent.   It is interesting to note that the smallest increase in numbers occurred in the two poorest soils (7A and 7B), and the greatest increase in the fertile nearly neutral soil (5B).

Cellulose in particular, affected an entirely different group of microörganisms than did the dextrose, although both are pure carbohydrates, free from any traces of nitrogen.   Cellulose is not attacked at all by most soil bacteria, but is very readily acted upon by numerous soil fungi.   Even in the case where there was an increase in the number of bacteria following the addition of cellulose, the great increase in the number of fungi makes us wonder whether the multiplication of bacteria is due entirely to the utilization of the cellulose directly or in part to the utilization of its decomposition products.   Where no nitrogen was added, the greatest increase of fungi and of bacteria took place in the fertile acid soil (5A), followed by poor acid soil (7A), for fungi, and by the poor neutral soil (7B), for bacteria.   When $NaNO_3$ is added, there was a ten-fold increase of the fungi in the fertile acid soil, over the soil to which no $NaNO_3$ has been added, and a thirty-fold increase in the poor acid soil. The addition of $NaNO_3$ brought about only a two-to three-fold increase in the number of bacteria over the numbers occurring where no $NaNO_3$ was added.   This again indicates the importance of the presence of available nitrogen for the development of fungi and for the decomposition of cellulose. The failure of the bacteria and actinomycetes to develop in the poor acid soil may be due to the original acid condition of the soil further slightly augmented by the acid formed from the cellulose by the fungi.

Straw contains a small amount of nitrogen (about 0.7 per cent), which may be sufficient for the needs of bacteria, but is not sufficient for an abundant development of fungi.   Practically the same development of bacteria took place in all soils, with or without the addition of available nitrogen.   The fungi, however, developed abundantly in the acid soils, but not in the limed soils; the addition of available nitrogen greatly increased the development of fungi (table 5) even in the case of straw.

Alfalfa increased the numbers of both bacteria and fungi to a much greater extent than did straw. Since alfalfa contains sufficient nitrogen (2.5 per cent) for the development of fungi, the addition of $NaNO_3$ effected no increase in bacteria, nor even in fungi.

Dried blood, containing 9.5 per cent nitrogen, added to the soil brought about an entirely different development of the microorganisms than did the substances poor in protein. The numbers of bacteria were greatly increased in all soils, which points again to the fact that bacteria prefer protein substances (outside of dextrose and other readily available carbohydrates) as sources of energy, while the fungi can thrive upon both proteins and higher carbohydrates at the proper reaction. Fungi developed most abundantly in the acid soils and to a lesser extent in the limed soils. The actinomycetes developed most markedly in the two well buffered acid soils (5A, 9A). The lack of development of actinomycetes in the two poor soils (7A, 7B) and in the limed fertile soil (5B) is probably caused by the ammonia formed in abundance from one per cent of dried blood added. This made the reaction so alkaline (pH = 9.0) in the two poor soils (poorly buffered) and in the neutral fertile soil that it repressed the development of actinomycetes, which are rather sensitive to extreme alkalinity as well as acidity.

SUMMARY

The observed effects of organic materials (dextrose, cellulose, rye straw, alfalfa meal, and dried blood) on the numbers of microörganisms in the soil, as determined by the plate method within three weeks after adding the materials, lead to the following conclusions:

1. All of the organic materials used greatly increase the numbers of microorganisms in the soil but not all to the same extent.

2. Some organic materials greatly affect one group of microörganisms but the others to a much less extent:

   a. Dextrose increases the numbers of bacteria in particular.

   b. Cellulose increases the numbers of fungi in particular.

3. Rye straw and alfalfa meal increase the numbers of fungi and bacteria.

4. Dried blood increases the fungi, bacteria and actinomycetes.

5. Additions of $NaNO_3$ to the straw treated soil further increase the numbers of fungi without affecting the numbers of bacteria. Nitrate additions greatly increase the development of microörganisms in soils treated with cellulose over those soils having no additions of nitrate.

6. Alfalfa increases the numbers of microörganisms to a greater extent than straw, while dried blood causes greater increases than both of these.

7. The numbers of fungi increase more abundantly in the acid soils than in those more nearly neutral in reaction.

8. The numbers of microörganisms reach a much higher point in the fertile than in the less fertile soils.

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MICROBIOLOGICAL ANALYSIS OF SOIL AS AN INDEX OF SOIL FERTILITY. IX. NITROGEN FIXATION AND MANNITE DECOMPOSITION[1]

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Various investigators have reported that a definite correlation exists between the capacity of the soil to fix nitrogen and soil productivity, and also between this capacity and other bacterial activities, such as nitrification.

Christensen (6, 7), using as an index the intensity of growth of raw cultures of Azotobacter in mannite solutions inoculated with soil, came to the conclusion that this relative growth can serve as an index of the calcium and phosphorus content of the soil. Löhnis and Pillai (16) concluded that the fixation of nitrogen in mannite solutions inoculated with soil, is an approximate measure of the fertility of the soil, especially as to its content of available minerals. There was, however, no strict parallelism between the laboratory results and crop yields. Similar results were obtained by Moll (17) and Pillai (19).

Brown (3, 4) found that the results obtained from studies of nitrogen-fixation in soils, taken from plots subjected to different rotations, correlated very well with the results secured in the ammonification and nitrification tests as well as with crop yields. Brown concluded, therefore, that the nitrogen-fixing power of a soil may indicate its relative crop-producing power. A remarkable correlation between the amount of nitrogen fixed in 100 cc. of sterile mannite solution containing 1 gm. of mannite and inoculated with 1 gm. of soil and incubated for three weeks, with the known fertility of the soil was also observed by Burgess (5). He suggested, therefore, that next to nitrification, nitrogen-fixation tests can be used as criteria of soil fertility. Azotobacter was present in the more fertile soils and absent in the soils of low productivity.

Given, Kuhlman and Kern (12) also obtained a correlation between nitrogen fixation, in a solution of 2 per cent mannite, and crop productivity of a series of plots. However, on repeating the same experiment, with another series of plots, very little correlation was obtained. Beijerinck (1) suggested recently that there is a definite parallelism between the number of Azotobacter cells in the soil and soil fertility.

Two methods have been commonly used for determining the capacity of a soil to fix nitrogen; viz., the solution method and the soil method. The solution method was introduced by Remy (20, 21, 22) and further developed by Löhnis (15), and others. As applied to the measurement of the power of a soil to fix nitrogen, this method consists of adding 5–10 gm. of soil to 100 cc. of a standard nitrogen-free sterile mannite solution, incubating for 7–30 days, and then determining the amount of nitrogen fixed. By the use of this method, the activities of the nitrogen-fixing flora of the soil are studied under standard conditions, while the influence of the various physical and chemical conditions of the soil upon the activities of the organisms in the particular soil is not considered. The soil method consists

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in adding a certain amount of energy material (1–2 per cent mannite or dextrose) to 100 gm. of fresh soil placed in tumblers or flasks; the optimum amount of moisture is then added and the tumblers are incubated at a definite temperature for 21–30 days, when the increase in total nitrogen is determined. The advantage of the soil method is supposed to consist in the fact that the fixation of nitrogen is studied under conditions similar to those that take place in a natural soil, where the activities of the organisms are more normal. Both of these methods are, of course, far from imitating natural conditions, since one can hardly imagine a soil to which 1 or 2 per cent of soluble organic nitrogen-free material is added. According to Green (13), the solution method proves to be valuable in the study of the fixation of nitrogen, while Brown (3) considered the soil method as an improvement over the solution method.

The underlying principle of the two methods, for the study of the fixation of nitrogen can thus be summarized as follows:

A source of energy, chiefly mannite or dextrose, is added to the soil or to a solution inoculated with soil. The amount of available nitrogen in the soil is very limited, so that the fungi and heterotrophic non-nitrogen fixing bacteria, which are capable of consuming rapidly the mannite or dextrose, cannot do that to a very large extent, since a minimum of nitrogen is required for their growth. The amount of dextrose or mannite used in the laboratory tests (1 to 2 per cent) is in great excess over the amount of available nitrogen, present in the soil or solution. Since the nitrogen-fixing bacteria can readily utilize mannite or dextrose and fix atmospheric nitrogen, in the absence of available nitrogen, the excess of the former will enable them to fix the nitrogen. This has been demonstrated by Waksman and Starkey (24), who found that cellulose and substances rich in cellulose, like straw, greatly stimulate the development of fungi, especially in the presence of available nitrogen. The addition of dextrose to the soil will not, however, greatly affect the development of these organisms, but will stimulate greatly the multiplication of bacteria, especially the nitrogen-fixing forms.

Lipman and Burgess (14) have shown that, with a proper supply of energy-producing materials, all agricultural soils may be made to fix atmospheric nitrogen, when inoculated into a properly constituted mannite solution; only a fraction of these soils, however, contain Azotobacter organisms; soils containing the latter possessed a greater nitrogen-fixing power. In this connection, the reaction of the soil, as expressed by its hydrogen-ion concentration, is of prime importance, both in influencing the development of particular types of nitrogen-fixing bacteria and in the amount of nitrogen that will be fixed per gram of mannite or dextrose consumed. At a pH value of 6.0 and above, Azotobacter will develop in the soil; at a greater acidity, other nitrogen-fixing bacteria, like the Clostridium group and perhaps the *B. aerogenes* and *B. asterosporus* groups, will develop. It seems that the latter are less efficient than Azotobacter in fixing atmospheric nitrogen. Gainey (11), for example, has demonstrated that out of 418 soils examined, 199 were found to contain Azotobacter; the average amount of nitrogen fixed, per gram of sugar, was 6.36 mgm. for all soils, 8.30 mgm. for those containing Azotobacter, and 4.61 mgm. for those not containing any Azotobacter.

The nitrogen-fixing bacteria are, however, limited in their activities by one mineral, which they require in excess over the others, namely phosphorus. Stoklasa (23), for example, has shown that the Azotobacter cells contain as much as 5 per cent P_2O_5. When an excess of mannite or glucose is added to the soil or solution, the Azotobacter, Clostridium and other nitrogen-fixing bacteria will make an extensive growth, using the available energy and deriving their nitrogen from the atmosphere. Since about one unit of available phosphorus (P_2O_5) is required for every two units of nitrogen fixed or assimilated by the organisms and synthesized into microbial protein, the supply of phosphorus may be a limiting factor. The actual amount of nitrogen fixed in the soil, especially by Azotobacter, may then become merely an index of the available phosphorus in the soil.

Dzierzbiczki (9) attempted to determine the need of phosphorus in the soil by the development of Azotobacter. Niklewski (18) added 10 gm. of soil to 100 cc. of a solution containing mannite, with or without soluble phosphate; the solution was sterilized either before or after adding the soil, and inoculated with Azotobacter. The following results were obtained:

Nitrogen fixed in 100 cc. of mannite solution + 10 gm. of soil

SOIL NEED OF PHOSPHORUS	SOLUTION STERILIZED BEFORE SOIL WAS ADDED		SOLUTION STERILIZED AFTER SOIL WAS ADDED	
	P_2O_5 in medium	No P_2O_5 in medium	P_2O_5 in medium	No P_2O_5 in medium
	mgm.	*mgm.*	*mgm.*	*mgm.*
None........................	8.22	5.35		2.85
Medium......................	5.48	4.08	14.51	1.95
Great........................	3.78	1.67	15.05	0.35

Stoklasa (23) used the following method for determining the need of the soil for phosphorus: 30 cc. of water containing 2.5 gm. of glucose, 0.2 gm. K_2SO_4 and 0.05 gm. of $MgCl_2$ were added to 100 gm. of soil; the soil was then sterilized and inoculated with Azotobacter. After 21 days of incubation, the total nitrogen and phosphoric acid were determined in·the soil. One hundred grams of soil was found to contain 0.103 gm. of P_2O_5 and 0.164 gm. of nitrogen in the inoculated soil and 0.110 gm. of nitrogen in the uninoculated soil. The amount of nitrogen fixed was, therefore, 0.054 gm. Since Azotobacter cells contain 10 per cent nitrogen and 5 per cent P_2O_5, 0.027 gm. P_2O_5 or 26.21 per cent of the total P_2O_5 in the soil had to be assimilated by Azotobacter. This is an index of the available fraction of phosphorus in the soil.

A very fertile soil containing 0.084 per cent P_2O_5 has shown, by the above method, that 48.8 per cent of the total phosphorus was available; a soil of medium fertility contained 26.21 per cent available P_2O_5 out of a total content of 0.103 per cent, while only 11.66 per cent of the P_2O_5 of a poor forest soil was available out of a total content of 0.090 per cent.

Christensen (7) employed a phosphorus-free mineral solution, containing some $CaCO_3$ and 0.3 gm. KCl, to which he added 10 per cent of soil (5 gm. of soil to 50 cc. of solution) and estimated, from the amount of Azotobacter growth, the amount of available phosphorus in the soil. But in view of the fact that there are only few soils which are capable of allowing the development of Azotobacter in phosphorus-free mannite solution, the test should be modified so as to be sensitive to smaller differences in the content of available phosphorus in the soil. This is accomplished by using a series of flasks (10 or 11) containing mannite solution and varying amounts of K_2HPO_4 (0.0005 to 0.005 mgm.) and record is made of the concentration of phosphorus at which Azotobacter development takes place and where it reaches a maximum. Different soils were found to behave differently in this respect, so that even this test did not give the absolute phosphorus requirement of the soil. However, abundant Azotobacter development in phosphorus-free mannite solution indicates that the soil does not need any phosphorus.

Christensen (8) has further shown that the power of a soil to decompose mannite depends. primarily on the differences in the chemical condition of the soil. In the case of neutral or alkaline soils, the power to decompose mannite depends on the presence of available phosphates. The speed of decomposition of mannite in neutral soils may indicate, therefore. the need of a soil in available phosphates.

The method used by Christensen (8) and finally modified by Bondorff and Christensen (2) was carried out as follows:

One hundred grams of air-dry soil and 2 gm. of mannite are well mixed, placed in tumblers and brought up to moisture with distilled water. After the tumblers have been allowed to.

stand undisturbed for 2–3 hours, the soil is well stirred with a glass spatula and incubation at 25°C. is started. At intervals of five days, 5 gm. of soil is withdrawn and allowed to air-dry; the air-dry soil is then weighed again and extracted for two hours, with occasional shaking, with 200 cc. of water. The extract is then filtered through paper and 10 cc., or an amount equivalent to 0.25 gm. of soil, is placed in a 400-cc. beaker with 50 cc. of 0.05 N potassium permanganate solution and 3 cc. of dilute (6:100) sulfuric acid. The beaker is placed in boiling water for twenty minutes. Fifty cubic centimeters of 0.05 N oxalic acid is then added and the solution is titrated with 0.02 N potassium permanganate solution. The number of cubic centimeters of permanganate solution required indicates the amount of organic matter (residual mannite + soluble soil organic matter).

These methods for determining the nitrogen-fixing as well as the mannite-decomposing power of a soil can thus be divided into four groups:

1. The addition of mannite (usually 1–2 per cent) to the soil, incubating for 15–30 days, under optimum conditions, then measuring the increase in the total nitrogen of the soil.

2. Inoculation of a mannite solution, usually containing phosphate, sulfate, $CaCO_3$ and 1–2 per cent mannite, with 1–10 per cent of the fresh soil, incubating for 15–30 days, then determining the amount of nitrogen fixed.

3. Adding 10 per cent of soil to a phosphate-free mannite solution and incubating, or sterilizing and inoculating with Azotobacter and incubating, for 20–30 days, then determining the amount of nitrogen fixed.

4. Proceeding as in the first method, but determining at intervals of five days, for a period of thirty days, the residual mannite or content of soluble organic matter, by the potassium permanganate method or by any other method.

All these methods are based upon the principle pointed out above that an excess of an available carbohydrate, like mannite, will stimulate only organisms that can rapidly decompose the excess of mannite and obtain their nitrogen from the atmosphere. These organisms, will, therefore, fix a definite amount of nitrogen (depending also upon the nature of the organism) for a definite amount of mannite decomposed. The first and the fourth methods should, therefore, give the same results, only the latter may prove to be more sensitive. But since a large amount of available phosphorus is required for an extensive development of the nitrogen-fixing bacteria, especially the Azotobacter, and since there is a more or less definite correlation between the phosphorus and nitrogen content of the Azotobacter cells, the only limiting factor to the development of Azotobacter and other nitrogen-fixing bacteria and to the fixation of nitrogen (if there is enough potassium and calcium, and if the reaction is favorable), is the amount of available phosphorus in the soil, as indicated by method 3. The second method would merely indicate the type of nitrogen fixing flora existing in the soil, under the particular circumstances. A critical study of these four methods was therefore undertaken.

EXPERIMENTAL

A series of plots, treated for the last fifteen years with different fertilizers, which have been used in the previous studies reported in this series, were also employed for the following investigations. The treatment of the plots as well as their carbon and nitrogen content and crop yield is given in table 1.

In the first experiment (table 2) on nitrogen-fixation by different soils the tumbler or soil method was used:

One hundred-gram portions of the different soils, sampled on August 24, 1922, were placed in tumblers, 1 gm. of mannite was added to each, the soils were well mixed and, after the moisture was brought to 50 per cent of the moisture-holding capacity, the tumblers were incubated at 25–28°C. for thirty days. The total nitrogen was determined in the original soil and in the soil receiving mannite, by the Kjeldahl method, using 5 gm. of air-dry sieved soil.

TABLE 1

Chemical condition of the soil and crop yields

SOIL NUMBER	TREATMENT*	NITROGEN CONTENT	CARBON CONTENT	REACTION 1922	CROP YIELD	
					1908–1922	1923 (corn)
		per cent	*per cent*	*pH*	*lbs.*	*lbs.*
5A	Minerals + manure	0.1463	1.73	5.5	69,300	6,108
7A	Untreated	0.0826	0.96	4.9	15,464	1,710
9A	Minerals + NaNO₃	0.0994	1.17	5.8	57,968	5,273
11A	Minerals + (NH₄)₂SO₄	0.1064	1.23	4.4	41,754	1,753
19A	Minerals only	0.0908	1.13	5.4	29,926	5,030
5B	Minerals + manure + lime	0.1428	1.74	6.7	59,754	6,478
7B	Lime only	0.0868	1.18	6.5	30,160	5,566'
11B	Minerals + (NH₄)₂SO₄ + lime	0.0952	1.10	5.9	61,906	6,440
19B	Minerals + lime	0.0924	1.18	6.4	35,930	6,043

*Minerals = Yearly applications of 640 pounds acid phosphate and 320 pounds of potassium chloride per acre.

Manure = 32 tons of cow manure per acre.

Lime = 2 tons of gound lime every 5 years.

NaNO₃ = 320 pounds NaNO₃ per acre.

(NH₄)₂SO₄ = An amount equivalent to 320 pounds of NaNO₃.

TABLE 2

Nitrogen-fixation in soils to which 1 per cent mannite has been added

SOIL NUMBER	NITROGEN IN SOIL ITSELF	NITROGEN IN SOIL + MANNITE
	per cent	*per cent*
5A	0.1463	0.1468
7A	0.0826	0.0784
9A	0.0994	0.0994
11A	0.1064	0.1076
5B	0.1428	0.1512
7B	0.0868	0.1316
9B	0.1020	0.1120
11B	0.0952	0.0952

Table 2 indicates that the only definite differentiation that we may obtain in reference to nitrogen-fixation in the soil by the tumbler method, is influenced

by the soil reaction. All the soils with pH values less than 6.0 gave no increase or only a very slight increase in total nitrogen, while those soils having pH values greater than 6.0 gave a decided increase in the amount of total nitrogen. It is interesting to note that this is the limit for the development of Azotobacter in soils, as shown by Gainey (10). However, this method of

TABLE 3

Fixation of nitrogen in 100 cc. mannite solution inoculated with 5 gm. of soil

SOIL NUMBER	CONTROL	INCUBATED	INCREASE IN NITROGEN
	mgm.	*mgm.*	*mgm.*
5A	8.20	10.80	2.60
7A	4.96	7.12	2.16
11A	6.28	8.93	2.65
19A	5.26	8.78	3.52
5B	7.86	17.00	9.14 ✱
7B	5.28	9.94	4.66
11B	5.24	12.53	7.29
19B	5.16	9.60	4.46

*Soil sampled June 26, 1923.

TABLE 4

Influence of quantity of soil upon the amount of nitrogen fixed in mannite solution

SOIL NUM-BER	JULY 14, 1923						SEPTEMBER 11, 1923					
	1 gm. of soil			5 gm. of soil			1 gm. of soil			5 gm. of soil		
	Total N in control	Total N in incu bated solution	N fixed	Total N in control	Total N in incu-bated solution	N fixed	Total N in control	Total N in incu-bated solution	N fixed	Total N in control	Total N in incu bated solution	N fixed
	mgm.	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*m,m*	*mgm*	*mgm.*	*mgm*	*mgm.*
5A	1.65	6.05	4.40	6.65	10.40	3.75	1.88	6.49	4.61	6.42	11.09	4.67
7A	1.00	4.90	3.90	3.40	6.20	2.80	1.24	5.38	4.14	4.53	8.93	4.40
9A							1.41	5.86	4.45	5.32	8.78	3.46
19A	1.28	4.50	3.22	4.80	8.40	3.60	1.44	5.76	4.32	4.48	8.50	4.02
5B	1.55	10.10	8.55	6.15	12.10	5.95	1.86	10.72	8.86	6.68	16.70	10.02
7B	1.27	6.90	5.63	4.75	9.10	4.35	1.28	5.52	4.24	4.74	8.60	3.86
11B							1.37	4.90	3.53	5.12	7.78	2.66
19B	1.26	4.50	3.24	4.70	8.20	3.50	1.36	8.64	7.28	4.98	10.08	5.10

determining the nitrogen-fixing capacity of the soil allows no further differentiation between the differently treated soils. Repeated experiments with the same method using 2 per cent of mannite gave similar results.

The solution method was found to give a different set of results, somewhat more applicable for differentiation of the soil, as shown in table 3, where

a typical experiment is reported. The solution used had the following composition:

Mannite.. 20.0 gm.
MgSO$_4$·7H$_2$O.. 0.2 gm.
K$_2$HPO$_4$.. 0.2 gm.
NaCl.. 0.2 gm.
CaCO$_3$.. 5.0 gm.
Distilled water.. 1000 cc.
Made neutral to phenolphthalein with NaOH

One hundred-gram portions of the sterile solution were placed in 250 cc. Erlenmeyer flasks, plugged, sterilized, inoculated with 5 gm. of soil and incubated for 15 to 30 days; the total nitrogen was then determined in the incubated solution + soil and in the check solution + soil.

Although the differences in the nitrogen-fixing capacity of the different soils were definite, they did not always correspond to the fertility of the soil. The correlation is much better in the limed plots (B), where the reaction is not as acid as in the unlimed plots (A). In the former, the order of nitrogen fixation is 5B, 11B, 7B and 19B. Table 1 shows that the crop yields of these respective plots were in about the same order. However, in the case of the unlimed soils, there is little differentiation, the soil of the most fertile plot 5A fixing less nitrogen that the soil of the most acid plot 11A and a trace more than the most unfertile soil 7A. There is no doubt, therefore, that this method can yield certain information on the microbiological condition of the soil, but it should be modified.

To determine the influence of the quantity of soil added to the mannite solution upon the amount of nitrogen fixed, 1 and 5 gm. quantities were used, as shown in table 4.

The results brought out in the above table tend to show that, although appreciable quantities of nitrogen are fixed in mannite solutions inoculated with various soils, we do not find any such sharp differentiation between the variously treated soils (especially in the case of unlimed soils), as was found by the methods previously studied, namely, numbers of microorganisms, nitrifying and CO$_2$-producing capacities. All the unlimed soils possess about an equal nitrogen-fixing capacity as determined by the solution method. This may be due to the fact that all of them contain a similar nitrogen-fixing flora (with the exception of the B plots, especially 5B and 19B which contain Azotobacter as well); when introduced into a favorable medium of the same composition, equal amounts of nitrogen are, therefore, fixed.

The following experiment was carried out with the idea of establishing whether any of the soil constituents, especially the phosphates affect the amount of nitrogen fixed. In this case the composition of the soil itself, especially its phosphate content, is made the variable factor, and the organism used for the fixation of nitrogen is the same. Ten-gram portions of the various soils (in a moist condition) were added to 100-cc. portions of the

liquid medium, with or without the phosphate; the flasks were plugged with cotton and sterilized at 15 pounds pressure for 1.5 hours. Some of the cultures were inoculated with *Az. vinelandii* and some were left as controls. After twenty days of incubation, the amounts of nitrogen fixed were determined, as shown in table 5.

TABLE 5

Influence of different soils and available phosphorus upon nitrogen fixation by Azotobacter vinelandii

SOIL NUMBER	NITROGEN FIXED WITH PHOSPHORUS PRESENT IN MEDIUM			NITROGEN FIXED WITH PHOSPHORUS ABSENT IN MEDIUM		
	Control	Incubated	N fixed	Control	Incubated	N fixed
	mgm.	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*
5A	8.78	18.36	9.58	8.78	16.42	7.64
7A	5.33	10.66	5.33	5.33	7.92	4.59
9A	7.06	13.68	6.62	7.06	13.25	6.19
19A	7.06	14.11	7.05	7.06	13.68	6.62
5B	9.30	21.17	11.87	9.30	13.39	4.09
7B	5.03	15.70	10.67	5.03	8.35	3.32
19B	6.91	17.28	10.37	6.91	9.07	2.16

TABLE 6

*Course of decomposition of 1 per cent mannite in soils of different fertility**

SOIL NUMBER	AFTER 2 DAYS' INCUBATION			AFTER 5 DAYS' INCUBATION			AFTER 7 DAYS' INCUBATION			AFTER 12 DAYS' INCUBATION		
	Soil alone	Soil + mannite	Difference	Soil alone	Soil + mannite	Difference	Soil alone	Soil + mannite	Difference	Soil alone	Soil + mannite	Difference
5A	7.8*	21.1	13.3	6.1	18.0	11.9	6.7	13.2	6.5	3.2	5.5	2.3
7A	7.9	21.2	13.3	4.7	17.7	13.0	6.3	18.0	11.7	3.1	15.8	12.7
5B	8.3	19.3	11.0	4.7	13.9	9.2	4.6	5.1	0.5	3.3	4.8	1.5
7B	4.5	18.9	14.4	9.6	20.1	10.5	4.5	15.7	11.2	2.1	11.7	9.6

*The figures in tables 6, 7, and 8 represent the cubic centimeters of 0.02 N permanganate solution used in neutralizing a solution, which was obtained by digesting 5 gm. of soil with 200 cc. of water, then digesting 10 cc. of the extract with 50 cc. of 0.05 N $KMnO_4$ solution, treating with 50 cc. 0.05 N oxalic acid and titrating with 0.02 N $KMnO_4$.

The soils which brought about the largest amount of nitrogen-fixation by Azotobacter, in the presence of phosphorus, namely 5B, 7B, 19B, have shown the lowest nitrogen-fixation in the absence of phosphorus. This becomes clear when we consider the crop yields for 1923. The samples were taken on September 29, just after the corn crop was harvested. Since larger yields were obtained on plots 5B, 7B and 19B than on the corresponding A plots, one would expect that these soils should contain less available phosphates at that particular period and, if this is the factor limiting the amount of nitrogen fixed, the above results would be expected.

In the last experiment, the amounts of mannite left in the medium were determined by the method of Christensen and were found to run parallel with the amounts of nitrogen fixed.

TABLE 7

Course of decomposition of 2 per cent mannite in soils of different fertility*

SOIL NUMBER	TREATMENT	INITIAL SAMPLE	AFTER 3 DAYS' INCUBATION	AFTER 13 DAYS' INCUBATION	AFTER 20 DAYS' INCUBATION	AFTER 35 DAYS' INCUBATION
5A		42.3*	33.2	30.8	25.7	13.0
7A		41.9	39.2	27.3	29.9	25.2
19A		49.8	38.3	29.1	30.6	26.1
5B		44.8	30.7	5.6	3.6	3.9
7B		43.2	35.0	26.1	24.2	17.3
11B		43.1	31.5	24.2	28.7	17.8
19B		43.1	33.0	21.8	29.7	26.6
7A	25 mgm. K_2HPO_4	41.9	33.9	23.5	23.6	16.8
7A	100 mgm. K_2HPO_4	42.7	26.0	23.6	20.5	7.8
7A	100 mgm. K_2HPO_4 + 100 mgm. $CaCO_3$	42.3	26.3	20.8	20.8	8.3

* See footnote for table 6.

TABLE 8

Course of decomposition of 2 per cent mannite solution in differently treated soils and the influence of available phosphates*

SOIL NUMBER	TREATMENT	INITIAL SAMPLE	INCU-BATED 3 DAYS	INCU-BATED 7 DAYS	INCU-BATED 13 DAYS	INCU-BATED 20 DAYS	INCU-BATED 31 DAYS
5A		41.0*	29.9	29.1	18.2	6.4	8.4
7A		39.5	33.2	37.5	33.3	32.0	26.5
9A		39.5	34.4	33.9	27.8	22.4	14.4
11A		40.1	33.0	32.3	29.2	23.0	22.4
5B		41.4	29.8	20.1	9.5	4.3	6.5
7B		42.0	29.2	26.6	12.7	4.1	7.4
11B		38.1	29.4	26.3	20.3	14.8	7.0
5A	25 mgm. K_2HPO_4	38.3	28.8	26.8	22.3	9.9	8.8
5A	100 mgm. K_2HPO_4	35.5	25.8	25.4	19.6	7.5	8.5
5A	100 mgm. $CaCO_3$	39.0	26.6	25.7	20.7	5.5	8.3
5A	100 mgm. $CaCO_3$ + 100 mgm. K_2HPO_4	35.1	26.7	24.7	16.7	5.6	8.0
7A	25 mgm. K_3HPO_4	39.1	30.0	33.9	31.3	30.8	21.3
7A	100 mgm. K_3HPO_4	40.4	31.3	32.2	27.0	26.2	14.3
7A	100 mgm. $CaCO_3$	42.0	28.7	31.2	27.2	26.8	15.0
7A	100 mgm. $CaCO_3$ + 100 mgm. K_3HPO_4	38.5	28.9	32.4	27.3	19.4	8.6

* See footnote for table 6.

To find whether the disappearance of mannite in the soil, as suggested by Christensen, may not prove to be a better index of the activities of the nitrogen-fixing bacteria than measuring the increase in nitrogen, 1 per cent man-

nite was added to a group of soils and the disappearance of mannite determined by the method of Bondorff and Christensen described above (table 6).

These results indicate that the fertile soils 5A and 5B, which contain sufficient phosphorus, decompose mannite very rapidly, especially the limed soil 5B; the unfertile soils 7A and 7B decompose mannite only slowly, especially
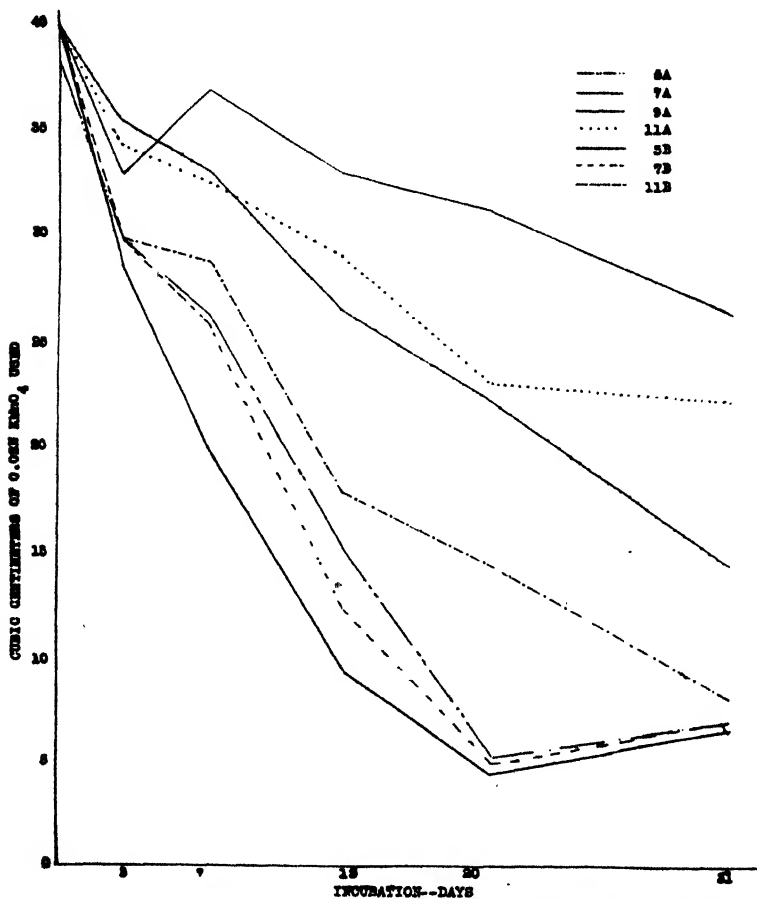
FIG. 1. COURSE OF MANNITE DECOMPOSITION IN SOILS OF DIFFERENT FERTILITY

the unlimed 7A. The experiment was repeated with a group of soils sampled on August 22, 1923, using 2 per cent mannite. To demonstrate whether the low mannite-decomposing capacity of 7A is due to the lack of phosphorus, to the acid reaction or to both, three groups of tumblers containing 100 gm. of soil 7A were treated (1) with 25 mgm. K_2HPO_4, (2) with 100 mgm. K_2HPO_4

and (3) with 100 mgm. K₂HPO₄ + 100 mgm. CaCO₃ . The results are given in table 7.

Soils 5A and 5B are thus found to be most active in decomposing mannite; these soils receive both minerals and manure and are otherwise also most
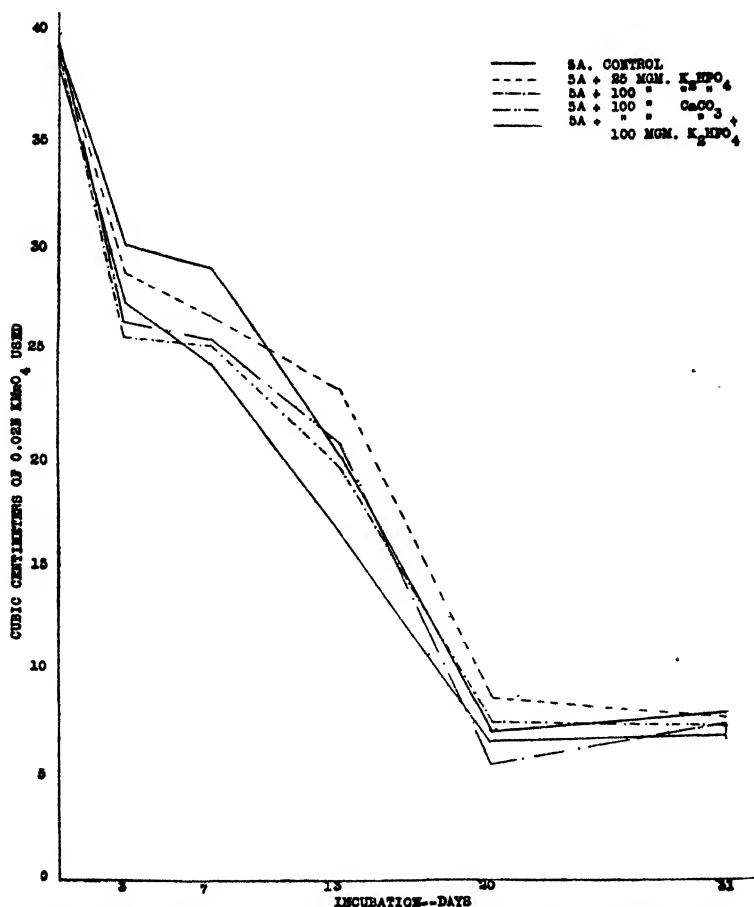
FIG. 2. INFLUENCE OF ADDITION OF SOLUBLE PHOSPHATE AND LIME TO A FERTILE ACID SOIL UPON ITS MANNITE-DECOMPOSING POWER

active biologically and most fertile. The most unfertile soil 7A, receiving no fertilizer or manure at all, and the soils receiving minerals only, but not nitrogenous fertilizer, were least active. The plots receiving lime only and lime, minerals and ammonium sulfate fell between these two groups of plots, in their mannite-decomposing power. The addition of 25 mgm. K₂HPO₄

to 100 gm. of soil 7A was sufficient to greatly increase its mannite decomposing power. The addition of 100 mgm. K_2HPO_4 brought about a still further action; the addition of $CaCO_3$ to this acid soil, however, did not result in any greater activity than the addition of the phosphate alone.
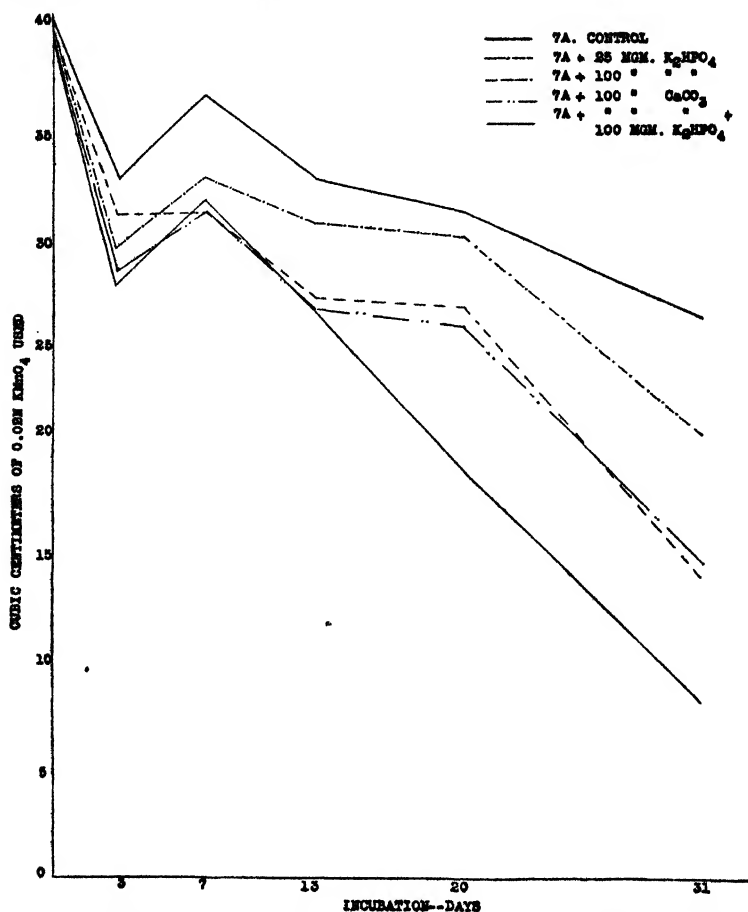
FIG. 3. INFLUENCE OF ADDITION OF SOLUBLE PHOSPHATE AND LIME TO AN INFERTILE ACID SOIL UPON ITS MANNITE-DECOMPOSING POWER

This question is further illustrated in table 8, where the results are presented of a study of the influence of soil treatment upon its mannite decomposing power and of the addition of phosphate or lime or both to a fertile soil (5A), not requiring any phosphate, and to an infertile soil (7A), greatly in need of available phosphate.

The most active mannite-decomposing soils were again those that have received minerals and manure; these were followed closely by the limed plot (7B) and the limed plot receiving minerals, lime and ammonium sulfate (11B). In other words, the limed plots are more active in decomposing mannite than the unlimed plots. The manured soils are leading both among the limed and unlimed, especially so in the unlimed soils. A definite correlation between the mannite-decomposing power and the crop yield for 1923, is thus obtained:

Mannite-decomposing power (decreasing order): 5A, 9A, 11A, 7A; 5B, 11B, 7B
Crop-producing power (decreasing order): 5A, 9A, 11A, 7A; 5B, 11B, 7B

The addition of phosphate as well as lime or lime and phosphate did not increase the mannite-decomposing power of 5A, showing that this soil does not need any available phosphate; the addition of phosphate or lime, and especially lime and phosphate together, to the unfertile soil 7A greatly increased its mannite-decomposing power; the addition of phosphate and lime to the most unfertile soil resulted in almost as high a mannite decomposing power as that found for the fertile soils. This is clearly brought out in figures 1, 2, and 3.

SUMMARY

The ability of a soil to fix nitrogen, when an excess of a readily available source of energy is added to it, depends upon the microbial flora of the soil, the physico-chemical condition of the soil, especially its reaction, and upon the presence of available phosphates and potassium salts.

It was found, as a result of the previous studies on the microbiological condition of the soil that the determination of numbers of microörganisms in the soil, nitrifying capacity, CO_2- producing capacity and cellulose-decomposing capacity help us to get an insight into the microbiological condition of the soil. The first tells us about numbers of different groups of microörganisms as affected by soil treatment; the second deals chiefly with the rapidity with which the soil nitrogen can become available; the third with the rapidity of decomposition of the soil organic matter and the fourth with the total available nitrogen in the soil. Next to nitrogen, the most important element in the nutrition of plants is phosphorus. None of the above four methods gives a direct indication as to the amount of available phosphorus in the soil. This can be done by the method discussed in this paper, namely by measuring the nitrogen-fixing or mannite decomposing power of the soil.

The determination of the nitrogen-fixing capacity of the soil, as a result of addition of mannite to the soil, is unreliable, due to the small amounts of nitrogen fixed and to the non-sensitiveness of the method for determining the total nitrogen in the soil. A study of the disappearance of mannite in the soil by the method suggested by Christensen is much more applicable.

Three methods can, therefore, be recommended for the determination of the nitrogen-fixing and mannite-decomposing power of a soil, with a view of obtaining information on the microbiological flora capable of fixing nitrogen and on the available phosphorus in the soil:

1. The common solution method, consisting in adding 1 or 5 gm. of soil to a standard mannite solution, incubating for 7 to 28 days, then determining the increase in total nitrogen above the control. This serves as an index of the nitrogen-fixing flora of the soil and to some extent of the microbiological condition of the soil.

2. The method suggested by Niklewski (18) and Stoklasa (23). This consists in adding 10 gm. of the particular soil to 100 cc. of 2 per cent mannite solution, free from available phosphates, sterilizing and inoculating with a vigorous culture of Azotobacter. After incubating for 20-30 days, the increase in total nitrogen is determined. This can serve as an index of the available phosphate in the soil.

3. The method for determining residual mannite (or rather soluble organic matter in the soil) suggested by Christensen (8). This consists in adding 2 per cent of mannite to the soil, incubating with optimum moisture, then determining the residual mannite, every five days, by oxidation with $KMnO_4$. This method as well can serve as an index of the activities of the nitrogen fixing flora and of the amount of phosphorus available in the soil.

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ALKALI SOIL INVESTIGATIONS: I. A CONSIDERATION OF SOME COLLOIDAL PHENOMENA[1]

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Most of the work on alkali soils has been directed toward a solution of the problems of removing the excess of alkali from the soils or neutralizing the harmful effects of these salts as by converting the black alkali into white and leaching out or scraping off from the surface the accumulated salts. Attempts have been made to determine the mode of formation of alkali soils, also the possible reactions involved when the soils are treated. Most attention, however, has been given to the study of the tolerance of various plants to concentrations of salts comparable to those found in alkali soils. In recent years some of the experiment stations, notably the California Station and some European investigators, especially in Russia, began a series of studies with the hope of revealing the nature and origin of the alkali soils and the reactions involved. It was recognized that a thorough understanding of these factors was necessary before any rational methods of treatments could be followed. One of the most important features of the recent investigations is the appreciation of the colloidal nature of some of the phenomena accompanying alkali soils.

In the course of an investigation conducted at the New Jersey station by the authors following up the suggestion of Lipman (13) to utilize the biochemical oxidation of sulfur for the amelioration of alkali soils the problem of the colloids has been considered. It was felt that a consideration of the alkali problem would be otherwise incomplete. Before we analyze the colloids in question it is necessary to review the general ideas on the subject of colloids within the realm of reactions directly related to those which may be manifested and demonstrated in the complex colloidal system of the alkali soils.

Gedroiz (5) discusses this problem. He states "The moist soil represents a dispersed system in which the soil solution is the dispersed medium and the soil organic and mineral particles are the dispersed phase. Such a system depending on the mechanical composition of the soil (degree of dispersion of the soil particles) possesses surface energy of varying degrees. Phenomena which take place in a dispersed system are subject to the fundamental law of colloid chemistry which states: 'Each dispersed system tends to decrease its free surface energy.' Since the surface energy equals the product of the total surface of the

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dispersed phase and the surface tension at the point of contact of the particles of this phase and the dispersed medium, the tendency of the system to decrease its surface energy consists in an effort to decrease the size of the total surface, e.g. decrease the degree of dispersion and the amount of surface tension of the dispersed medium. In the case of soils the latter applies to the soil solution. . . . . There are substances which will decrease the surface tension of water, for example acetic acid or most of the organic acids and bases, substances of high molecular structure, (like the alkaloids and dyes). There are also substances which will increase the surface tension, such as inorganic salts, acids and bases and organic substances with a high hydroxyl content, like sugars. These substances, however increase the surface tension in rather less degree than those that decrease the surface tension. The effort of the dispersed system to decrease the surface tension as outlined may be accomplished by the change in concentration of the substances in that layer of the dispersed medium which is indirectly adjoining the surface of the dispersed particles; if with the increase in the concentration of a dissolved substance, the surface tension of the water is de-

TABLE 1

Surface tension of extracts of treated and untreated alkali soils at various incubation periods

SULFUR TREATMENT PER ACRE	SURFACE TENSION AT		
	22°C. after 15 days	19°C. after 75 days	19°C. after 190 days*
pounds	*dynes*	*dynes*	*dynes*
None	63		
None	69	71.0	71.0
2,000 S	73	72.42	
2,000 T	73		
4,000 S	73		73.13
4,000 T		72.42	
6,000 S	73	74.5	74.5
6,000 T	72.3	74.5	74.5
4,000 c.p. alum	71.58 *		73.8

S = Sulfur applied to surface 4 inches.
T = Sulfur mixed with bulk of soil.
*These extracts were made up from unleached soils; all others were from leached soils. The cultures from this series were incubated at room temperature. They consisted of 3 pounds of alkali soil with the various treatments in earthenware glazed pots, one quart capacity with holes on the bottom to facilitate leaching. A detailed description will be found in a subsequent publication.

creased, then on account of the efforts of the system—soil + solution of such substance— to decrease the surface tension, the substance in question (let us say, acetic acid) will concentrate in the layer of water at the surface of the particles. This is spoken of as adsorption on the surface of the soil particles. The solution of such a substance mixed with soil will be heterogenous at various places in the system; if we consider two neighboring soil particles, we find that at the surface of the particles we have the most concentrated solution and as we move away from the particles approaching their mean center the concentration of the solution is lowering. The phenomenon of the increased concentration of a dissolved substance in a layer of the dispersed medium indirectly adjoining the particles of the dispersed phase is known as *positive adsorption*. Substances which increase the surface tension of the dispersed medium cause the reverse phenomenon—*negative adsorption;* solutions of such substances with the increase in concentration increase the surface tension; the effort of the dispersed system to decrease the surface energy is accomplished

through a lowering in concentration of the dissolved substance in the layer of the dispersed medium adjoining the particles. Thus with substances of the first group (which decrease the surface tension) the dispersed phase attracts to its surface from the dispersed medium the dissolved substances (positive adsorption); with substances of the second group (which increase the surface tension) repulsion of the dissolved substances takes place (negative adsorption)."

The above considerations are supported by the well known theorem of Gibbs in the thermodynamic consideration of adsorption phenomena, and may be summed up in the citation of Lewis (12, p. 304).

"Gibbs showed, as a thermodynamical necessity, that if a dissolved substance had the property of lowering the surface tension of the solution the substance would exist at a higher concentration in the surface layer than in the bulk of the solution."[3]   The theoretical considerations of Gibbs' theorem have a bearing on the physical adsorption of the soil particles. Positive adsorption protects the soil from leaching out the easily soluble substances. On the other hand negative adsorption has the reverse influence. In the alkali soils the reduction of positive adsorption and increase of negative adsorption is of prime importance. One of the problems of reclamation of alkali soils is the washing out of the soluble salts. This is facilitated by a decrease of the positive adsorption. This may be accomplished by decreasing the size of the total surface of the dispersed phase. The coagulation of the colloids is therefore a step in this direction. The soils where coagulation took place the capillary rise of the water increased as shown later, the permeability also increased, the surface tension of the soil extracts increased, thus favoring negative adsorption.

Table 1 gives the data on the surface tension of the alkali soil extracts. In general it is known that suspensoids hardly alter the surface tension; on the other hand colloid solutions increase or decrease the surface tension depending on the colloid. According to Ostwald (16) gum arabic or starch increase the surface tension of water while gelatin, glue, egg-albumin decrease. The data in table 1 show that the colloids in the alkali soil extract decrease the surface tension;[4] this increases positive adsorption and prevents the leaching of alkali soils; on the other hand the oxidation of sulfur increased the surface tension most and thus increased negative adsorption which is favorable for leaching. The alum treatment also increased the surface tension but in less degree than the products of sulfur oxidation. As a result of the change in surface tension and decrease of the total surface of the dispersed phase the negative adsorption is tremendously increased. The physical condition thus changed,

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[3] Those interested in a more detailed discussion of this theorem will find helpful the mathematical expression of Gibb's theorem:

$$\Gamma = - \frac{c}{RT} \cdot \frac{d\sigma}{dc}$$

where Γ equals the excess of the dissolved substance in the dispersed medium per unit surface of the dispersed phase as compared with what would have been in the absence of this surface; c = concentration of the dissolved substance in the dispersed medium; T = absolute temperature; R = the gas constant; σ = surface tension; $\frac{d\sigma}{dc}$ = the differential, expressing increase or decrease of surface tension with the increase of concentration of the dissolved substance. The deduction of this equation was made by Freundlich (see Lewis 12, p. 305).

[4] The apparatus used for the surface tension determinations was that of du Nouy (15).

causes greater permeability and allows the leaching of soluble salts. The expression of this phenomenon may be found in the rate of leaching or in the rise of capillary water. Figures 1 and 2 give the curves of a series of soils treated as outlined in table 2. These two sets of curves represent two different incubation periods,[5]—one after 14 days, the other after 95 days. It will be noted that after 14 days the differences in capillary rise are not great. All cultures showed practically the same rate of rise of water. The cultures treated with alum have total rise greater than any other. This indicates that the strongly adsorbed trivalent aluminum ion exerted its influence by coagulating the colloids and thereby decreasing the surface. As we turn our attention to figure 2 an entirely different picture presents itself; the outstanding fact is the rise of the capillary water in the cultures treated with sulfur. On the other hand, the curve for the culture treated will alum no. 8, runs alongside the

TABLE 2

Treatment of alkali soils and the rate of leaching after 95 days incubation

LABORATORY NUMBER OF CULTURE	TREATMENT PER ACRE	AMOUNT LEACHED AFTER	
		7 hours	48 hours
		cc.	*cc.*
1	None..	40	75
2	4000 pounds sulfur..........................	97	285
3	4,000 pounds sulfur + 5 tons peat...........	190	298
4	6,000 pounds sulfur.........................	197	290
5	6,000 pounds sulfur + 5 tons peat...........	167	293
6	2,000 pounds sulfur.........................	42	90
7	2,000 pounds sulfur + 5 tons peat...........	68	150
8	4,000 pounds c.p. alum + 5 tons peat	44	138
9	4,000 pounds c.p. alum + 2,000 pounds sulfur..	80	210
11	5 tons peat.................................	00	53

untreated or the peat culture. The effect which was apparent after 14 days of incubation gradually disappeared upon further incubation. This is very significant and the discussion of such behavior of the alum will be found later when the coagulation of colloids is taken up. The same may be said about culture 9 which is manifesting the effects of the combined alum and sulfur treatment. In general it is evident that the cultures treated with sulfur have undergone pronounced surface influences allowing greater permeability and therefore a greater rise of the capillary moisture. Table 2 gives some figures on the rate of leachings. While the phenomenon of capillary rise of moisture is an indirect criterion for the change of surface due to the coagulation of the colloids and change in surface tension the data on the leaching are a direct criterion. The data on the rate of leaching after 95 days is very typical for all the series of experiments which will be reported presently. The soils treated with sulfur

[5] The whole series of capillary studies will be reported in the paper following.
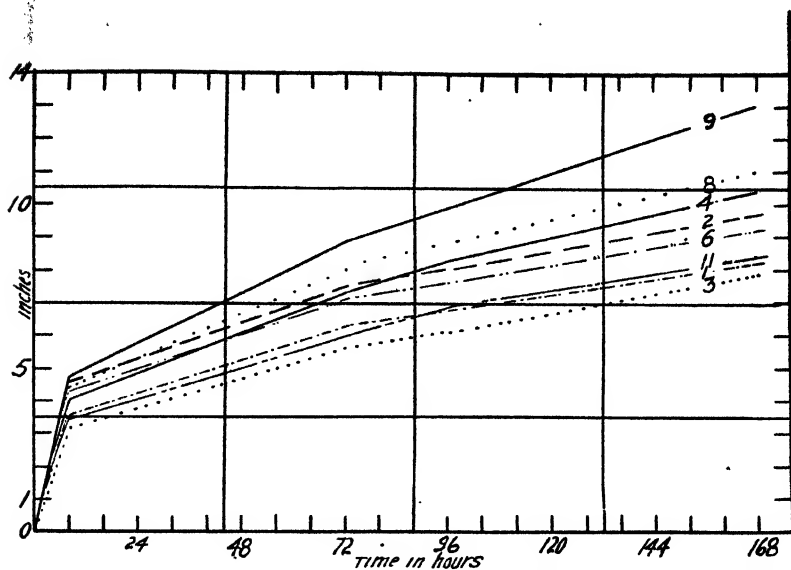
FIG. 1. CURVES SHOWING RISE OF CAPILLARY WATER IN FIRST SERIES AFTER 14 DAYS' INCUBATION

Numbers indicate treatment as outlined in table 2
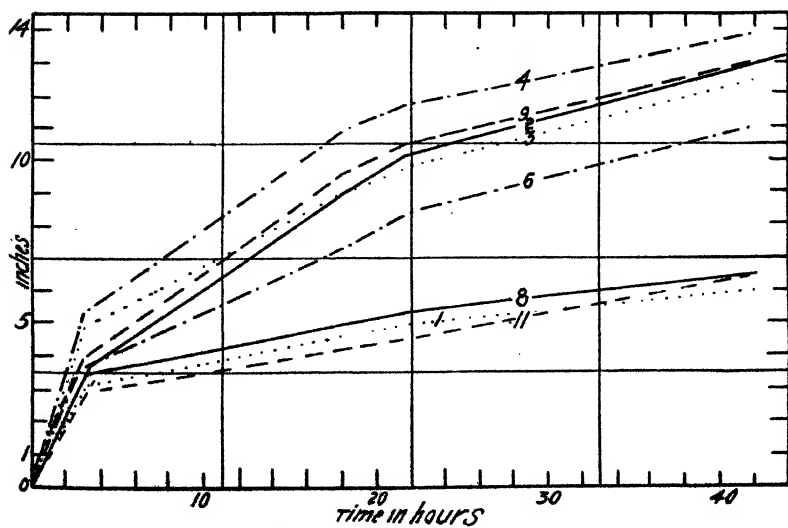
FIG. 2. CURVES SHOWING RISE OF CAPILLARY WATER IN FIRST SERIES AFTER 95 DAYS' INCUBATION

became most permeable to water, allowing rapid leaching. In many instances even after 6–7 days of contact culture 1, untreated, or culture 8 treated with alum, had water on the surface. This water was either poured off or allowed to evaporate. Attention must be called again to the beneficial effects of the treatment with sulfur and alum combined, in culture 9.

The cultures subjected to leaching consisted of 1.4 pounds of alkali soils in flower pots; 400 cc. of water was applied to the surface. A more detailed account of the experiment will be given in the subsequent papers where the analyses of the leachings and extracts will be presented in full.

All of these considerations are based on the theorem of Gibbs, but we must remember that Gibb's expression in its entirety is applicable under conditions where chemical effects and solubility of the solute in the adsorbing phase are reduced to a minimum (11, p. 305). This is true in the case of charcoal. However, it is doubtful whether the chemical effects of the soil solution in contact with the soil particles are negligible. This must be borne in mind in considering the phenomenon of positive and negative adsorption in soils. In general, however, the forces of physico-chemical adsorption based on Gibb's theorem must be accepted as playing an important part. The work of Langmuir (11) also seems to show that adsorption may be looked upon as purely chemical phenomenon.

Coming back to the coagulation of the colloids we shall consider the forces which tend to accomplish this desirable process in alkali soils.

COAGULATION OF COLLOIDS

One of the important generalizations of colloid chemistry is the one dealing with the coagulation of colloids by electrolytes. This generalization is known as the Hardy-Schulze Law and reads as follows: "Ions carrying a charge of sign opposite to that carried by the colloid are the most active precipitants, and at the same time the higher the valence of the ion (i.e. the greater the number of unit charges upon it) the greater its precipitating action." If the colloid is positively charged then, of course, the negative ions of high valence are the most effective precipitants, the reverse is true with colloids negatively charged. Besides coagulation by electrolytes, colloids may also be coagulated by heating or cooling the colloidal solution or by electrolysis (more correctly speaking by cataphoresis), the particles being carried in virtue of their charge to one of the electrodes where they become discharged and assume the gel form. The adsorption of cations or anions (depending on the charge of the colloid) is of importance in coagulation of colloids. The lower the valence the more it is adsorbed, although it is not always the case. In a recent paper, Chatterji and Dhar (2) show that pure manganese dioxide will adsorb 0.0015 equivalents of silver but only 0.00033 of barium or 0.0001 of aluminum. This would indicate that the charge is the determinative factor. In speaking of coagulation we must remember that the hydrogen ions of acids, even though

monovalent, have a coagulation power equal and sometimes greater than that of divalent or even trivalent metals.   This fact should be kept in mind as we shall see the effect of coagulation power of the hydrogen ions of the sulfuric acid formed by the biochemical oxidation of sulfur in alkali soils.   The hydrogen ion introduced into a dispersoid is of extreme importance in the coagulation of colloids as we shall see presently.

TABLE 3

Effect of alum, sulfuric acid or a combination on the coagulation of colloids in alkali soil extract

TUBE NUMBER	TREATMENT			REACTION OF SUPERNATANT LIQUID	RELATIVE AMOUNT OF COAGULATION	INTENSITY OF COLOR IN SUPERNATANT LIQUID
	0.01 M alum	0.1 M H$_2$SO$_4$	1.0 M NaOH			
	cc.	cc.	cc.	pH		
1	1		0.8	9.0*	Considerable	Slight
2	1		1.0	9.2*	Very slight after 24 hours	No apparent change
3	1		1.1	9.3*	None	No apparent change
4	1		2.0	9.6*	None	No apparent change
5	1			4.8	Practically instantaneous	Clear as water
6	0.5			6.0	Heavy	Very slight
7	0.3			7.0	Heavy	Very slight
8	0.2			7.0	Appreciable	Slight
9	0.1			7.4	Slight turbidity; slight precipitate after 24 hours	No apparent change
10		2		3.0	1†	8†
11		3		2.8	2	5
12		4		2.6	3	4
13		5		2.4	4	3
14		7		2.0	6	2
15		8		2.0	7	1
16	0.05	1		6.0	0	10
17	0.1	2		3.0	3	4
18	0.15	3		2.6	7	2
19	0.2	4		2.4	9	1
20				9.2	0	10

* The potentiometer was used for these readings.

† The intensities of coagulation and color for tubes 10–20 are indicated by numerical values expressing comparison with the control, tube 20.

Experiments were conducted to ascertain the coagulating effect of sulfuric acid and alum respectively on the colloids of alkali soil extracts.   At the same time the reaction at which coagulation takes place was also investigated.   For that purpose 25-cc. portions of untreated alkali soil extract were placed in test tubes and various additions of sulfuric acid and alum solutions were added. Table 3 gives the plan and results of the experiments.

It will be noted that the alum treatment is most efficient in coagulating the colloids.   However, not until the reaction reaches pH 7.4 does the alum begin to show its coagulating power.   At pH 7.0 we get heavy coagulation, although the rate of coagulation is delayed.   That not all the colloids have been precip-

itated may be judged from the persistence of some color in the supernatant liquid. It is remarkable that at pH 4.8 (tube no. 5) the rate of coagulation was practically instantaneous. This would suggest that it is the isoelectric point at which any colloid is most unstable as pointed out by Hardy (7, 8). In this connection it is appropriate to recall the work of Loeb (14) who shows that the isoelectric point of gelatin is at pH 4.7. In tube 1 with the pH 9.0 there was only some coagulation even though the amount of alum added was the same as in tube 2. This would indicate that the reaction has some effect on the coagulating power of any substance. On the other hand, tube 3 shows that at pH 9.2 and above the alum has no coagulating power. Of course we must remember that in these cases the presence of the peptizing agent is of prime importance in the stability of sols. It has been shown recently by Thomas and Johnson (18, 19) that precipitation (coagulation in our case) is due to removal of peptizing agents by chemical action between them. In our case the addition of the NaOH means an increase in the peptizing agent and thus stability of the colloid sols. From the data on the combination of alum and sulfuric acid it seems as though the reaction plays no important rôle in the coagulation of the colloids in this particular case; tube 16 with a pH reading of 6.0 showed no effects even after a prolonged standing of seven days. At the same time, tube 6 showed heavy coagulation immediately after addition of the alum. Unquestionably the trivalent aluminum ion is responsible for the coagulation effect, whether by ionic neutralization of electric charges, by selective adsorption, or both. Of extreme interest is the combined effect of the alum and sulfuric acid. Taking tubes 9 and 17 and comparing the effects we note that no. 17 had appreciable coagulation and the color intensity changed markedly; on the other hand no. 9 had only very slight coagulation and no apparent change in coloration. Still the amount of alum added was the same in both cases. Tubes 19 and 8 are comparable in the same sense. The differences may be due to the hydrogen-ion concentration variant; this explanation may find its support in some of the figures as pointed out. It is more likely, however, that we have here an entirely different phenomenon. In dealing with coagulation effects we must consider both the cations and anions and more so the mutual effect of two cations or anions. By adding H_2SO_4 and alum we do not modify the anion effect of the alum, since both anions are the same, but we introduce a different cation. If one cation has a coagulation power equal to x and another the coagulation power equal to y, the combined cations have not a coagulation power equal to their algebraic sum $x + y$. Generally the combined effect is greater than the sum. The increase is not in an arithmetic progression. Such an effect could be noticed in the combined effects of alum and sulfuric acid. The curves on the capillary rise in figures 1 and 2 prove the same thing.

From what has been said it is logical to conclude that in the coagulation of colloids the quantitative relationships of the colloids precipitated should follow the same tendency, namely that with alum and sulfuric acid more of the col-

loids should be precipitated than with either ingredient singly. With this in view 50-cc. portions of alkali soil extract from untreated soils were taken and treated in the manner given in table 4. It is significant that the precipitate of tube 5 carried more iron and silica than any other treatment. Undoubtedly we have here the combined effect of the aluminum and hydrogen-ion. It is also worth while to note the reaction at which most of the colloids precipitate. Again the probable isoelectric point played its part. These experiments were repeated with variously treated soils and the results were very similar. We need not go into a more detailed discussion of this complicated subject; for our purpose it will suffice to accept with reservation the law of Hardy and Schulze in relation to coagulation.[6] It is known that the colloids in soils are negatively charged although there is the possibility of a high iron and aluminum colloidal sol content which are positive. In order to prove that the colloids in the alkali soil extract (untreated) are negatively charged the routine experiments in colloid chemistry for the determination of the charge was

TABLE 4

Effect of alum and sulfuric acid on colloids precipitated

| NUMBER OF TUBE | TREATMENT | | REACTION | KMnO₄ FOR Fe TITRATION | SiO₂ |
	0.01 M alum	0.1 M H_2SO_4			
	cc.	*cc.*	*pH*	*cc.*	*mgm.*
1	2		4.7	1.25	1.0
2		2	8.4	*	*
3	1	1	6.4	1.25	0.8
4	0.5	1.5	7.4	0.9	0.9
5	1.5	0.5	4.8	1.80	1.5

*No precipitate was formed.

carried out. The procedure was as follows: An arsenic trisulfide sol was prepared by mixing equal volumes of a 1 per cent arseneous acid solution (dissolved by boiling and filtered cold) and distilled water saturated with H_2S. The mixture was boiled for over one-half of an hour to drive off the excess of the H_2S. An iron oxide sol was prepared by pouring 5 cc. of a concentrated ferric chloride solution into 500 cc. of boiling water and continuing to boil for a few minutes. The colloidal solution was then poured into collodion bags and dialyzed in distilled water until practically none of the peptizing agent could be detected in the distilled water. The alkali soil extract was made up by mixing 50 gm. of soil in 500 cc. of distilled water, shaken for several hours and left over night undisturbed. The supernatant liquid was decanted and centrifuged for 1.5 hours at high speed (1000 revolutions per minute). The clear liquid was

[6] The authors are aware of the remarkable researches of Loeb as summarized by him (14). It matters little whether the effects are viewed in the light of stoichiometric considerations as Loeb suggests, or from the viewpoint of Freundlich's and others adsorption theories.

then ready for use; 80 cc. of arsenic trisulfide and iron oxide sols were poured separately into 100 cc. graduated cylinders and to them 20 cc. of the alkali soil extract was added. The mixture was shaken and allowed to be undisturbed. The iron oxide sol after 10–15 minutes began to settle while the arsenic trisulfide sol did not settle at all even after 10 days. This is sufficient proof to show that the alkali soil extract colloids are negatively charged, since the arsenic trisulfide being also negatively charged had no effect. On the other hand the positively charged iron oxide sol caused coagulation. In this connection it is worth while to mention the work of Gordon and Starkey (6) who claim that adsorption of soils is influenced more by iron and alumina colloids than by silica colloids. This may indicate that the chief colloids are iron and alumina and these as a rule are positively charged. This is contrary to the general idea of the charge on soil colloids. There can be no question about the charge of the colloids in alkali soils as shown above.

What then, are the effects of these colloids on the soil properties and how are they modified by coagulation?

In soils the chief colloids are of silica, iron, aluminum, clay and organic materials. The silica colloids are negatively charged and are resistant to precipitants; even metals of high valence have but little effect on their precipitation in soil. This has been pointed out by Ehrenberg (3) and others. The failure of Gordon and Starkey to get adsorption by silica colloids may be due to this property of the silica colloids. This is important inasmuch as in the alkali soil extract silica colloids are quite in abundance and have a protective effect on the other colloids as will be shown presently.

The colloids of the organic substances are known as humus colloids. These colloids are also negatively charged and in alkali soils they exist in the hydrosol form due to the peptization of the organic matter, the peptizing agent being the sodium carbonate.[7] These colloids perhaps also have a protective effect on the other colloids. The dark brown color of alkali soil leachings is due to the humus colloids. This color is changed upon coagulation with the sulfuric acid formed from the sulfur oxidized; it becomes a pale straw colored liquid.

The hydrated iron oxide colloids are present in soils in greater or smaller degree depending on amount of iron present in the soil; this in turn is influenced by the native minerals. In the alkali soil they are invariably present. The charge of this colloid is positive. The coagulation may be accomplished by the negatively charged anions and also by the negatively charged colloids: This latter subject of mutual precipitation will be dealt with later.

The hydroxide of aluminum is undoubtedly present and behaves somewhat similar to the iron. The clays are degradation products of the silicates and are formed just as the hydrated iron oxide colloids by the hydrolysis of water soluble salts. Clays behave both like an electro-negative and electro-positive

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[7] As the oxidation of sulfur progresses and carbonates disappear the peptization of organic matter cannot take place. As the organic colloids are coagulated they do not appear in the leachings and serve as buffers.

colloid depending on conditions. It is possible that the electro-negative behavior of clays is due to protective effects, although a reverse in charge of colloids is not uncommon. Biltz (1) succeeded in coagulating clay with the electro-negative silicic acid colloid. And besides the hydrogen-ion concentration of the dispersed medium has an effect on the charge.

It would lead us too far if we should go into a discussion of the possible reactions due to the colloids. We shall confine ourselves within a limited range of phenomena which manifest themselves in the alkali soils.

It has already been pointed out that any colloid system tends to decrease its free surface energy and this may be accomplished by decreasing the surface tension and by decreasing the total surface. This is determined in a great measure by the size of the dispersed phase. Now the surface of any soil has an effect on the rate of evaporation, since the latter is essentially a surface phenomenon. In soils with a high colloid content the decrease of the dispersed phase will decrease the surface and thus reduce the rate of evaporation, as the latter is more rapid the larger the surface. Keen (9) has shown that, since the vapor pressure influences greatly the rate of evaporation, the colloidal properties of the soil having in turn an effect on the rate of evaporation (due to increase of surface) will thus influence the vapor pressure. In alkali soils with its high colloidal content the coagulation of the colloids decreases its surface and thus should decrease evaporation.

Experiments to ascertain the rate of evaporation as effected by the vapor pressure are complicated in nature and due to the lack of facilities such experiments could not be carried out as planned. Evaporation experiments carried out as shown presently were not satisfactory, still there were indications pointing toward a greater evaporation from the *surface* of soils where the degree of dispersion, as in the case of non-treated soils, is great. On the other hand with the coagulation of the colloids and thus a lowering of the degree of dispersion, as in the case of the soils treated with sulfur or alum, the evaporation is slower from the surface.

Beakers of uniform size were selected, 50 gm. of the alkali soils of treatments as previously described were placed in them and weighed. After 10 cc. of water was added to each, the beakers were again weighed; after 24 hours they were weighed again and loss compensated. After that the beakers were weighed at intervals of time, 5 hours, 18 hours, 24 hours and 42 hours. The reason for allowing the soils to be in contact with water for 24 hours previous to taking the readings was to give the soil a chance to come to its normal condition inasmuch as the drying has an effect on the condition of the colloids going from sol to gel state and vice versa.

It is worth while to record that evaporation from unleached soils was always greatest in the untreated soils in the earlier periods, e.g. after 3, 4, 6 hours. After a more prolonged period evaporation was faster from the treated soils. The changes produced in the dispersoid of the soil due to the various treatments affected the amount of surface and probably also the vapor pressure of the

soil solution. Extracts from the soils as shown in table 5 show very little depression of the freezing point and thus also of the vapor pressure. The latter was determined by calculating the molar concentration in the extracts from the freezing point depression. Then the well known formula of Raoult $\dfrac{P - P_1}{P} = \dfrac{n}{N}$ was applied. P = the vapor pressure of the solvent, P_1 = the

TABLE 5

Lowering of freezing point and vapor pressure of alkali soil extracts at various incubation periods

	FIRST SERIES				SECOND SERIES				
	14 days		140 days			75 days†		190 days	
Treatment per acre	Freezing point lowering	Vapor* pressure	Freezing point lowering	Vapor pressure	Treatment per acre	Freezing point lowering	Vapor pressure	Freezing point lowering	Vapor pressure
	°C.	mm. Hg	°C.	mm. Hg		°C.	mm. Hg	°C.	mm. Hg
None	0.065	17.352	0.05	17.3545	None	0.042	17.3559	0.06	17.3528
4,000 lbs. S	0.067	17.3517	0.06	17.3528	2,000 lbs. S‡	0.02	17.3596		
4,000 lbs. S ⎫ 5 tons peat ⎭	0.062	17.3525	0.072	17.3508	2,000 lbs. S§			0.052	17.3542
6,000 lbs. S	0.062	17.3525	0.048	17.3549	4,000 lbs. S‡			0.052	17.3542
6,000 lbs. S ⎫ 5 tons peat ⎭	0.064	17.3522	0.062	17.3525	4,000 lbs. S§	0.022	17.3592		
2,000 lbs. S	0.062	17.3525	0.067	17.3517	6,000 lbs. S‡	0.002	17.3626	0.067	17.3517
2,000 lbs. S ⎫ 5 tons peat ⎭	0.062	17.3525	0.043	17.3557	6,000 lbs. S§	0.016	17.3603	0.074	17.3505
4,000 lbs. c.p. alum ⎫ 5 tons peat ⎭	0.067	17.3517	0.052	17.3542	4,000 lbs. c.p. alum ⎭	0.01	17.3613	0.067	17.3517
4,000 lbs. c.p. alum ⎫ 2,000 lbs. S ⎭	0.068	17.3515	0.062	17.3525	Original extract; not incubated ⎭			0.082	17.3491
5 tons peat	0.059	17.353	0.052	17.3542					

* Vapor pressure given is at 20°C.; the vapor pressure of water at this temperature is 17.363 mm.

† Extracts were made up from soils previously leached. All others were from unleached soils.

‡ Sulfur was applied to surface 4 inches.

§ Sulfur mixed with bulk of soil.

= vapor pressure of the solute, n = the number of moles of solute, N = the number of moles of solvent per liter (for H_2O = 55.52). It is significant that the original soil extract depressed the vapor pressure most. The fact that the treated soils allow more intense evaporation after six hours is therefore not due to the vapor pressure, as far as the extract data is concerned, but to other causes. It is very likely that the treatments which change the permeability

and coagulate the colloids also produce better aeration, and that the greater evaporation after six hours is due to that factor.

Another very important consideration in connection with the properties of colloids and their relation to alkali soil treatment is the effect of colloids on the permeability of the soil. The impermeability of alkali soils is a well known condition. When water is applied to alkali soils it does not penetrate the soil for a long time. The capillary rise of the water is also very slow as brought out by the data on capillary studies conducted at the various incubation periods in treated and untreated alkali soils. Kellerman (10) attributes the impermeability of certain Nevada soils to the presence of colloidal silica. The same idea is expressed by Scofield (17). However, it is quite possible that other colloids, especiallly the organic, play an important part. It may be that the phenomenon of impermeability in alkali soils is similar to that of hard pan and that the colloids serve as a cement at periods of drying out of the soils. The conversion from sol to gel and vice versa at various stages of moisture content will accentuate the condition. At any rate alkali soils have a sponge effect, holding the water after they take it up. · The capacity of colloids to hold or absorb large amounts of water is a well known phenomenon in colloidal chemistry. After treatment with a coagulating agent such as alum or sulfuric acid the permeability of the alkali soil is greatly improved. The degree of improvement goes hand in hand with the coagulation of the colloids; the more the colloids are coagulated the better is the permeability.

In normal soils the colloids serve as retentive agents of various constituents, retarding leaching. In alkali soils this colloidal property is, as pointed out, a hindrance reducing permeability, aeration and increasing the retentive power and thus the accumulation of salts after drying.

Mutual coagulation of colloids is well known and is likely to occur in soils which contain side by side the positive iron and aluminum colloids with the negatively charged silica and organic colloids. The recent work of Freundlich and Nathansohn (4) seems to show that even colloids of the same charge precipitate each other. It is also true that the quantitative relationships of the respective colloids have a great deal to do with their mutual coagulation. In the alkali soil extracts we have been able to demonstrate the preponderance of negatively charged colloids and the question arises what becomes of the positively charged iron and aluminum? It is suggested by the authors that there must be some protective effect. The silica or organic colloids, being negatively charged protect the positively charged iron colloids, which are not, however, coagulated by the oppositely charged silica colloids. It is also possible that even the iron and aluminum colloids have changed their charge after going through the isoelectric point. In the experiments to determine the charge in the alkali soil colloids as reported above, the amount of silica colloid coagulated was also determined. It was found that the addition of the positively charged hydrated iron oxide colloid coagulated more than 25 per cent of the silica.

In the next article the origin of alkali soils will be discussed, and data on the methods used for the amelioration of these soils will be presented and critically discussed.

SUMMARY

Positive and negative adsorption in the system—soil and soil solution—are of great importance in leaching out soluble substances.

In alkali soils, negative adsorption is desirable.

Coagulation of colloids increases the surface tension of the extract and modifies the physical condition of the alkali soils. These changes are manifested in the capillary rise of water and permeability of soils to water.

The effect of alum and sulfuric acid or both on the coagulation of alkali soil colloids was investigated. The effect of alum and sulfuric acid in combination is greater than that of either one separately. At pH 4.7 coagulation is practically instantaneous, pointing to the possibility of this being the isoelectric point.

The colloids of alkali soils are negatively charged and are precipitated therefore with positively charged colloids, or electrolytes with cations of high valency.

The dispersed phase affecting the surface, influences evaporation. The vapor pressure of alkali soil extracts is changed but little due to various treatments.

The nature of the impermeability of alkali soils and the protective effect of colloidal silica and organic colloids are discussed.

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THE IMPORTANCE OF HYDROGEN-ION CONCENTRATION CONTROL IN PHYSICO-CHEMICAL STUDIES OF HEAVY SOILS

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The extent of the recent literature on the measurement of hydrogen-ion concentration and its application to almost every branch of chemistry is evidence of the importance of hydrogen-ion concentration control (8). It is of especial importance in reactions of weak acids or bases and their salts such as occur in soils. Most of the numerous soil studies, in which the hydrogen-ion concentration has been considered, fall into one of six groups:

1. Studies of the variations in the pH value of natural soils, including the effect of the water content and of drying upon that value.

2 The relation of the hydrogen-ion concentration of soils to plant distribution.

3. The effect of the pH value of the soil upon that of the juices of plants growing on it.

4. The effect of the pH value of the soil upon the microbiological activities in it.

5. Titration curves in which the effect of additions of acids or bases upon the pH value is measured.

6. Studies of the relation of the pH value of the soil to its lime requirement as determined by the numerous lime requirement methods.

In much of the work on the effect of chemical treatments upon the flocculation of soils and upon the absorption and exchange of bases by soils, however, the importance of hydrogen-ion concentration control has not always been fully appreciated. Recent work in this laboratory and elsewhere indicates that the hydrogen-ion concentration existing after the soil and the treatment have reached equilibrium is one of the most important factors in determining the course of the reaction. This paper will treat only this type of investigation.

FLOCCULATION

The hydrogen-ion has long been known to be an effective flocculant for colloidal clay. The rôle of the hydroxyl ion has not been so clear. Maschhaupt (19) and others have shown that small amounts of an alkali tend to stabilize soil suspensions while larger amounts cause flocculation. Comber (9) found that clay suspensions were flocculated most readily in an alkaline mixture but he did not give its pH value. He estimated the flocculating power of different electrolytes, however, by observing the rate of settling of the coagulum formed by a decided excess of the electrolyte. Numerous observations

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in this laboratory (3) as well as those of Smith (25), Arrhenius (1), Burton (7), and others show that the addition of certain electrolytes in excess of the minimum required for flocculation, yields a coagulum that settles more slowly than if just enought is added to flocculate the colloid. This may be the reason for the apparent differences in the results of Comber and Maschhaupt. Tartar and Gailey (31) and Michaelis and Hirabayashi (22) have pointed out the importance of hydrogen-ion concentration control in the flocculation of mastic sols and have shown that many of the so-called "specific effects" attributed to the ion of the same charge as the colloid would disappear if the different electrolytes having the same cation were compared at the same Sörensen value.

The studies made in this laboratory (4) furnish convincing evidence of the necessity of hydrogen-ion concentration control if we are to obtain an adequate conception of the phenomena of flocculation in soils. All of the work reported here has been done on the colloidal fraction of the soils, separated by the method developed in this laboratory (3). These colloidal clay solu-

TABLE 1

Results with acids

ACID	MILLIEQUIVALENTS REQUIRED	pH WITH COLLOID	pH WITHOUT COLLOID	DIFFERENCE
HCl................................	0.48±0.02	3.9	3.5	0.4
H₂SO₄.............................	0.50±0.02	3.9	3.5	0.4
H₃PO₄ (as monobasic acid).............	0.73±0.016	3.7	3.3	0.4
H₃PO₄ (as tribasic acid)................	2.20±0.05	3.7	3.3	0.4
Acetic............................	5.5 ±0.5	3.8	3.7	0.1
Citric.............................	6.5 ±0.5	3.2	3.1	0.1

tions were comparatively uniform in the size of their particles, ranging between 20 and 80 milli-microns in diameter. They were very stable having but very slight tendency to settle out by gravity alone. Studies on their probable chemical nature indicate that they are composed largely of complex alumino-silicates. The minimum electrolyte requirement was determined by the usual trial and error method, observations being taken twenty-four hours after mixing the electrolyte with the clay. The results with a series of acids as given in table 1 show that while the minimum requirement varies as much as ten-fold if expressed in terms of milliequivalents per liter, or total titrable acidity, ranging from 0.48 of a milliequivalent for hydrochloric acid to 5.5 milliequivalents for acetic acid. All the acids, except perhaps citric, flocculate at approximately the same pH value, which in the case of this acid clay is about 3.8.

A series of mixtures having the same potassium content and varying in pH value between 3 and 13 gave the results plotted in figure 1. Curve 1 was obtained with an acid colloidal clay and curve 2 with a neutral clay. The

values for the acid clay are very significant. The electrolyte requirement increases gradually as the hydrogen-ion concentration decreases until the neutral point is approached then rises very quickly to a constant value. Variations in Sörensen values between about pH 8.5 and pH 12 had no effect whatever upon the minimum electrolyte requirement. Solutions made up of nine parts KCl and one part KOH flocculated at the same concentration of potassium as solutions of KOH alone, although ten times as much KOH was required as with KCl alone. This sudden increase at the neutral point in
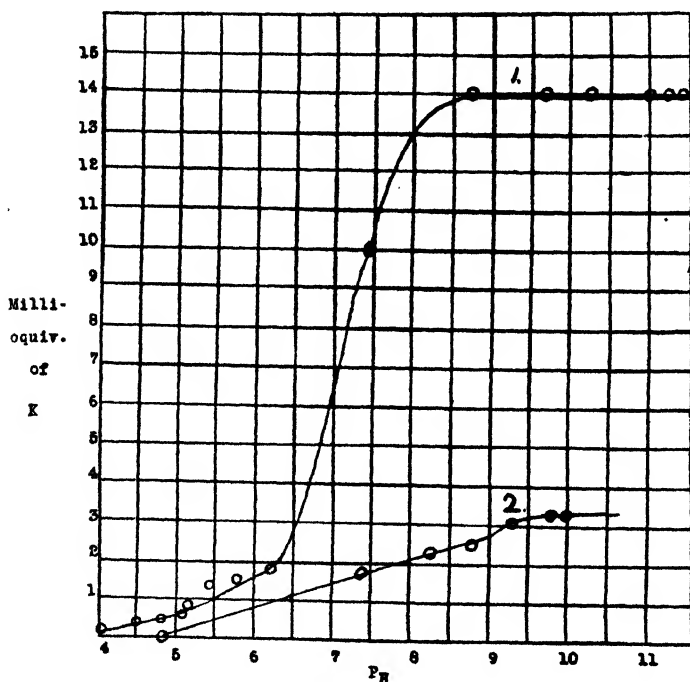
FIG. 1. THE EFFECT OF H-ION CONCENTRATION UPON THE FLOCCULATION OF AN ACID (1.) AND A NEUTRAL (2.) COLLOIDAL CLAY

case of the acid soil indicates that the alkaline mixtures have one function more than the other mixtures. They must neutralize the acid clay, then flocculate the resulting potassium salt of the clay. The acid clay seems to be neutralized before the pH value of 9 is reached, since from that point on further increases in alkalinity are without effect. If the sudden increase in electrolyte requirement near the neutral point in the case of the acid clay is due to the fact that a part of the KOH in the mixtures is used up in converting the acid clay into its potassium salt, a neutral clay should show no marked

change in electrolyte requirement at the neutral point. Curve 2 on figure 1 was obtained with a clay having a pH value of about 7. As would be expected the steep region of the curve is almost entirely lacking. Several other acid and neutral clays were studied and the above curves were found to be typical of their respective classes. The flocculating power of a series of calcium mixtures of varying Sörensen values was found to vary in the same way. The amount of calcium required in each case was, of course, considerably smaller probably because of the greater insolubility of the calcium-aluminosilicates formed.

Comber (9) found that $CaCl_2$ was superior to $Ca(OH)_2$ for flocculating very dilute clay suspensions but that the reverse was true for more concentrated suspensions. If the sudden increase in the electrolyte requirement of the acid clay at the neutral point in the experiment above was due to the fact ' that part of the KOH was utilized in neutralizing the acid clay, we would expect that the amount of the change at this point would be in proportion to the amount of acid to be neutralized, or in other words, to the concentration of the colloidal clay. Preliminary results obtained by Marshall and Powell in this laboratory indicate that this is true. The data plotted in figure 2 shows that as the concentration of the acid clay becomes greater the amount of potassium required for flocculation in the alkaline region also increases. These values were obtained by centrifuging immediately after the electrolyte had been mixed with the colloid and consequently the absolute amounts required are somewhat higher than in the previous series.

In much of the work on the flocculation of clay the valence of the electrolyte has been considered the most important factor. The results presented here indicate; (1) that the electrolyte requirement of a clay with any electrolyte can only be defined with reference to a definite pH value, (2) that the reaction of the clay determines the general type of curve obtained, (3) that the concentration of the clay is an important factor especially with alkaline flocculants, (4) that while the amount of various acids required for flocculation varies widely if expressed in total or titrable acidity, they all flocculate at about the same concentration of hydrogen-ions.

THE EFFECT OF HYDROGEN-ION CONCENTRATION UPON THE ABSORPTION AND EXCHANGE OF BASES

One of the earliest experiments that we have on the absorption and exchange of bases contains results which, in all probability, are due to differences in hydrogen-ion concentration. Thompson (32) in 1845 found that the amount of calcium and magnesium liberated from soils by $(NH_4)_2SO_4$ was in every case considerably greater than the amount liberated by $(NH_4)_2CO_3$ while the amount of NH_4 absorbed was greater in the case of $(NH_4)_2CO_3$.

Lemberg (16), in 1870 working on silicate minerals, found an equivalent exchange of bases between minerals and solutions of neutral salts. With

alkaline solutions the free base was absorbed without any appreciable exchange of bases. A few years later in 1877, Van Bemmelen (2) made his classic studies on absorption by colloidal gels. Like Lemberg, he found that solutions having an alkaline reaction, either the free hydrate or the alkaline salts of weak acids, such as H_2CO_3, H_3PO_4, $H_2B_2O_7$, were absorbed more strongly by soils and by silica gel than the neutral salts of the same metals. With the alkaline solutions there was no appreciable exchange of bases. The alkaline salts of the weak acids were converted into the corresponding acid salts. With neutral salts, however, an equivalent exchange of bases was frequently observed.
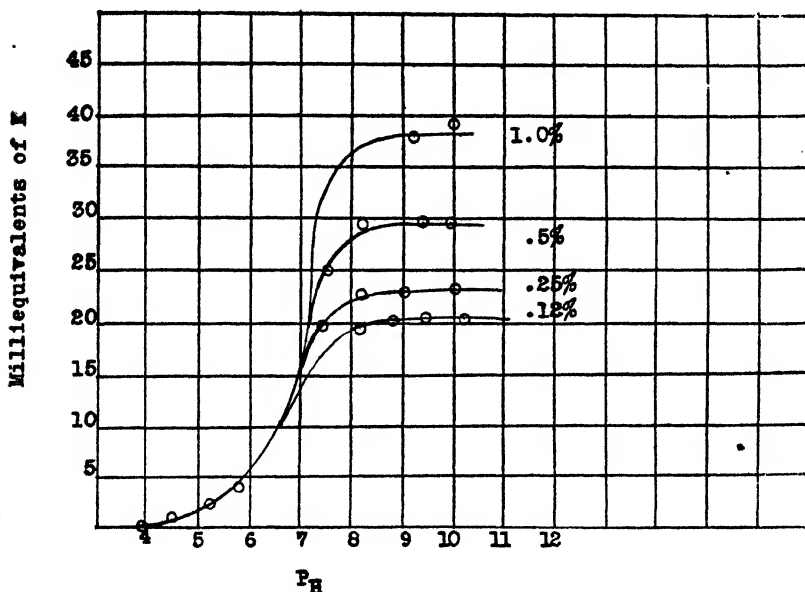
FIG. 2. THE EFFECT OF THE CONCENTRATION OF AN ACID COLLOIDAL CLAY UPON THE MINIMUM ELECTROLYTE REQUIREMENT WITH POTASSIUM MIXTURES AT DIFFERENT pH VALUES

Thirty years later Sullivan (29) studied the effect of a large number of salts upon a variety of silicates. In most cases some exchange of bases occurred but it was quantitative only in case a neutral mineral was treated with a neutral salt. The reaction of the mineral and of the salt solution used seemed to be the most important factors in determining the equilibrium. Unfortunately, we do not have very exact knowledge of the Sörensen value of his mixtures. The same criticism can be applied to much of the more recent work in spite of the fact that ready means of estimating the pH value of our mixtures are now available. In much of this work our knowledge of

the properties of the chemicals used and of the reaction of the soil enables us to see in a rough way how the hydrogen-ion concentration effects the equilibrium between chemical treatments and the soil. A typical case will be cited.

In his interesting study of base exchange in acid soils, Robinson (24) found that the supernatant liquid obtained by treating the acid soil with a 0.1 N solution of potassium acetate, contained much more titrable acid than that obtained with KCl or KNO$_3$. The acetate solutions contained in every case less salt after contact with the soil, while those of KCl and KNO$_3$ showed more.
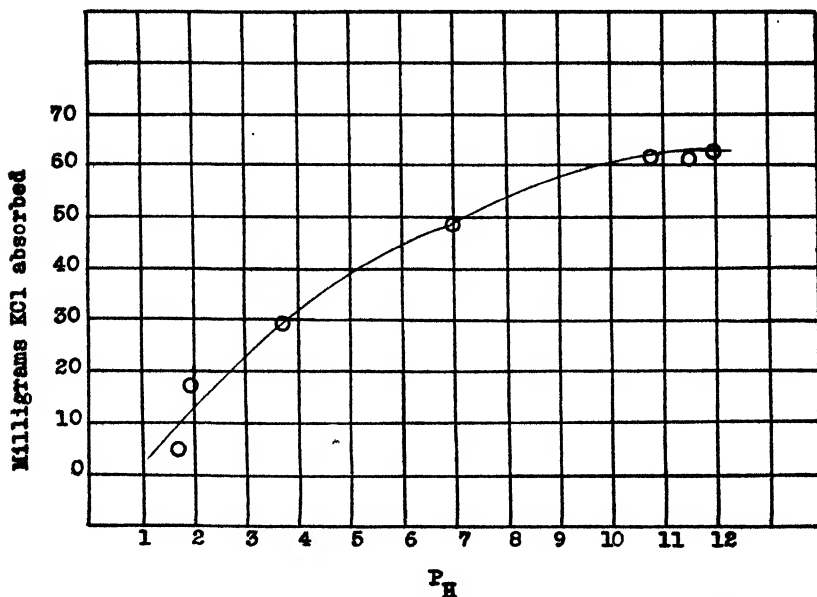
Fig. 3. The Effect of the Hydrogen-ion Concentration upon the Amount of Potassium Absorbed by One Gram of an Acid Colloidal Clay from .1 N Potassium Mixtures

We know that a potassium acetate solution is alkaline because of hydrolysis, and that a solution of KCl in equilibrium with an acid soil has a lower pH value than the soil itself. This would seem to indicate, as suggested by Robinson, that the differences might be due largely to the pH value at which equilibrium was established. If this assumption is true it should be possible to get similar results with KCl and mixtures of KCl and KOH combined in such proportions as to keep the potassium concentration constant and to gradually increase the pH value up to that of KOH. Such a study has been made in this laboratory using an acid colloidal clay and 0.1 N mixtures of KCl and KOH. The results are plotted in figure 3. As was anticipated,

the amount of potassium absorbed—as measured by the amount still in solution after equilibrium with the soil had been reached—increased almost linearly with the degree of alkalinity until a Sörensen value of about 10 was reached, then at a slower rate indicating that the saturation capacity for bases was being approached. A like study in which mixtures of $CaCl_2$ and $Ca(OH)_2$ were used has been made in this laboratory by Cowan and similar results obtained. Starkey and Gordon (28) report similar results for the absorption of potassium by silica gel. Swanson (30) has recently reported almost identical results in his study of the effect of reaction upon the adsorption of calcium by soils.
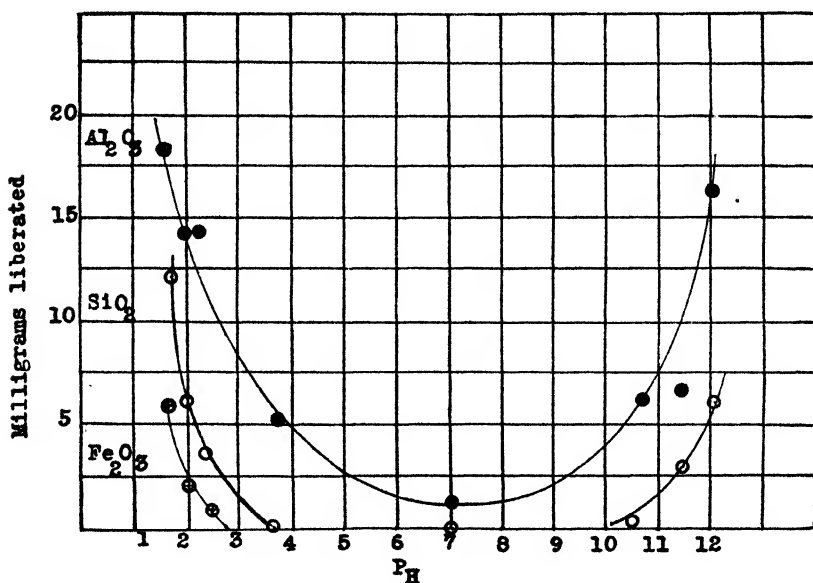
FIG. 4. THE EFFECT OF THE HYDROGEN-ION CONCENTRATION UPON THE LIBERATION OF Al_2O_3, Fe_2O_3 AND SiO_2 FROM AN ACID COLLOIDAL CLAY BY .1 N POTASSIUM MIXTURES

Analyses of the solutions for the other elements of the colloid made soluble by the mixtures of KCl and KOH also indicate the importance of pH control. The relationship for Fe_2O_3, Al_2O_3, and SiO_2 is shown in figure 4. The curves are all similar in the acid region. The solubility decreases with a decrease in the hydrogen-ion concentration and becomes negligible around the neutral point. With further increases in alkalinity, SiO_2 and Al_2O_3 are again made soluble. The curves obtained by Cowan with mixtures of $CaCl_2$ and $Ca(OH)_2$ are of the same type. The values for the calcium and magnesium liberated by the mixtures of KCl and KOH are given in figure 5. There seems to be no appreciable exchange of these bases in the more alkaline re-

gion.   The solubility of the calcium in the alkaline mixtures was not the limiting factor, for Ca(OH)₂ could be added to the alkaline solutions in quantity without precipitation.   Some evidence has been obtained which indicates that potassium may be liberated by Ca(OH)₂ if considerable more of the base is added than is needed to neutralize the acid clay.

If all the bases liberated are converted into their KCl equivalents, and the resulting values subtracted from the corresponding values for the amount of KCl absorbed, a curve can be obtained which will show the balance of bases at the different pH values.   Figure 6 was obtained in this way.   The values
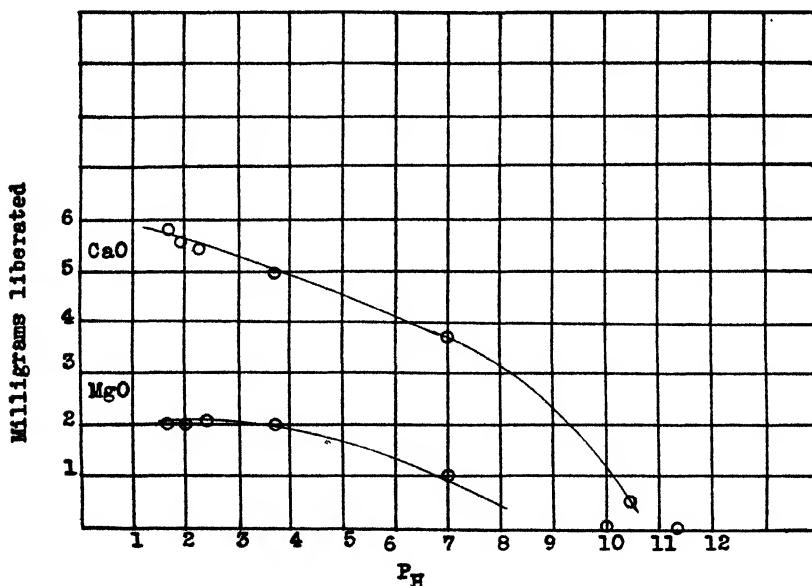
FIG. 5.   The Effect of the Hydrogen-ion Concentration upon the Liberation of CaO and MgO from 1 Gram of an Acid Colloidal Clay by .1 *N* Potassium Mixtures

below the zero ordinate indicate that more cations have been liberated from the clay than have been exchanged or absorbed, equivalent exchange occurred at the zero ordinate, while those above this ordinate indicated that more base was absorbed than exchanged.   It is interesting to note that the pH value at which the curve crosses the zero ordinate is the same as that of the clay.

Hissink (12) has pointed out the difficulty of determining the total base-absorbing capacity of a soil.   The investigations cited above point out a reason for this complexity.   The base-absorbing capacity of a soil can only be determined with reference to the hydrogen-ion concentration at which equilibrium between the soil and the salt or base has been reached.   Hissink

(13), Swanson (30) and others have shown that there is no close correlation between the normal pH value of a soil and its base-absorbing capacity. The clay content of a series of soils is a better index to their relative absorptive capacities than their pH value. It is the titrable or potential acidity of a soil that determines its power for holding bases and this may have but little relation to the original pH value. McGeorge (20) has recently reported that
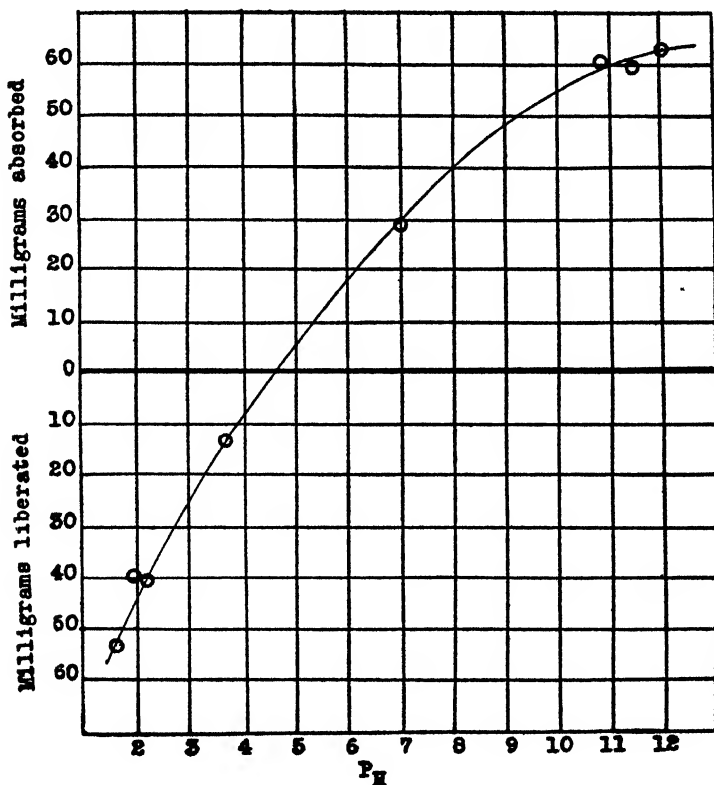
FIG. 6. THE EFFECT OF THE HYDROGEN-ION CONCENTRATION UPON THE TOTAL BASES LIBERATED OR ABSORBED BY AN ACID COLLOIDAL CLAY BY .1 *N* POTASSIUM MIXTURES. RESULTS CALCULATED ON BASIS OF KCl EQUIVALENT

two soils having an identical pH value, 5.98, differed by ten tons $CaCO_3$ per acre in their titrable acidity as determined by the Veitch method.

Since the absorptive capacity of a soil for bases is greatly influenced by the concentration of hydrogen ions at which equilibrium is established, it is clear that the only proper way to compare the absorbing capacity of two soils is to measure that capacity at a definite hydrogen-ion concentration.

The failure to control this important variable has led to many disputes. The question of the liberatin of soil potassium by calcium has been investigated by scores of chemists and opinions vary widely. Plummer (23) in summarizing the literature before the American Society of Agronomy in 1921 stated that "all the experiments made have failed to show that basic compounds of calcium and magnesium increase by chemical action to any practical extent the solubility of the soil potassium." MacIntire (18) likewise concludes as a result of extensive lysimeter studies that "economical applications of burnt calcareous, burnt dolomitic, ground calcareous or ground dolomitic limestone will not effect a direct chemical liberation of native soil potassium" although he did obtain some liberation of potassium with excessive applications of these basic limes. Similar results were obtained by Lyon (17). Tressler (33), however, in his work on the same soil as was used by Lyon, found that while potassium was not liberated by $CaCO_3$, it was liberated by applications of $CaSO_4$. Erdman (10) and numerous others have reported similar results. A survey of the recent literature, including over a score of independent investigations, indicates then that in neutral or acid soils, basic salts like $CaCO_3$ do not liberate soil potassium unless employed in great excess, while acid or neutral salts, like $CaSO_4$, do liberate appreciable quantities of potassium when applied in relatively small amounts. The importance of hydrogen-ion concentration control in such studies is quite evident.

The data presented in figure 6 indicates that all of the types of reaction noted by Van Bemmelen (2), Sullivan (29), Spurway (27) and others can probably be observed with any neutral or acid soil with any of the common bases and their salts by proper adjustment of the hydrogen-ion concentration Any treatment which will increase the hydrogen-ion concentration of a soil will lower its capacity for holding bases because of the substitution of hydrogen-ions for the metallic ions. If the hydrogen-ion concentration of a soil is not changed by the treatment equivalent exchange of bases is to be expected. If the soil is more alkaline after the treatment, indicating that hydrogen-ions have been neutralized and replaced by the cation of the hydroxide, less than equivalent exchange will be observed. If just enough alkali is added to neutralize the acid it will be largely absorbed without basic exchange, while if a decided excess is added basic exchange may again be obtained. These views are in harmony with the mass law.

Let us consider the results to be expected from additions of $CaCO_3$ and $CaSO_4$ from this point of view. Calcium added as $CaCO_3$ acts as a base and neutralizes the residual acidity in the soil thus raising its pH value. Since calcium ions replace hydrogen ions in the colloid complex there is no appreciable liberation of bases until the acidity is practically all neutralized. When calcium is added in the form of $CaSO_4$ to a neutral or acid soil the hydrogen-ion concentration of the mixture is either unchanged or slightly lowered, consequently there is an approximately equivalent exchange of bases.

THEORETICAL DISCUSSION

That the hydrogen-ion concentration exerts a profound influence in all physico-chemical studies of soils is a fact not to be questioned. When considering the probable theoretical mechanism of the observed facts, however, there may still be differences of opinion. Michaelis (21) has suggested that the surface molecules of a colloidal particle may be dissociated. Langmuir (15) considers adsorption as due to purely chemical residual valences. Hissink (14) and Van der Spek (26) are inclined to attribute the equivalent exchange of bases to chemical forces acting at the surface of the colloidal particle. Gordon (11) has presented a similar explanation for the behavior of silica gels. The work done in this laboratory on the colloidal fraction of acid clays shows (a) that standard hydroxide solutions when titrated with the acid clay solutions, give titration curves characteristic of weak polybasic acids by either the conductivity or the hydrogen electrode method (5); (b) that equivalent amounts of different bases are required for neutralization; (c) that the hydrogen-ion concentration of concentrated solutions of colloidal clay varies in the same way on dilution as with ordinary weak acids (6).

These studies seem to be further evidence of the chemical nature of the reactions of colloidal clay when coupled with the work reported in more detail above on (a) the relation of the hydrogen-ion concentration to the flocculation of an acid and a neutral clay, (b) on the effect of the concentration of the colloidal clay upon the variation in the amount of electrolyte required for flocculation at different Sörensen values, and (c) on the effect of the hydrogen-ion concentration upon the absorption and exchange of bases. Many results commonly cited as evidence against this conception may be attributed to the failure of the investigator to consider (a) the original reaction of the soil, (b) the hydrogen-ion concentration resulting after the soil and treatment have reached equilibrium with each other, and (c) the total or titrable acidity of the soil which is a complex function in which specific surface may play a larger rôle than the Sörensen value of the untreated soil.

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ABSTRACTS OF SOME PAPERS ON SOILS AND PLANT PHYSIOLOGY PRESENTED OR PUBLISHED IN 1923

RUSSIA[1]

A convention of the Russian investigators in soil science with the participation of geo-botanists, was held in Moscow during September 10–15, 1923. The following were elected as members of the Presidium of the All-Russian Convention; K. D. Glinka; A. A. Yarilov; N. M. Tulaikov; V. V. Hemmerling; Y. N. Afanasiev and B. A. Keller.

Thirty-five papers were presented, twenty-eight on questions of soil science and seven on geo-botanical subjects. A large number of the papers were devoted to questions of soil cartography; the others were devoted to the origin of soils, the study of properties of soils, methods of chemico-mechanical analysis, etc. Abstracts of some of the papers presented at the convention are given below.

On the Moisture Properties of the Soil. A. F. LEBEDIEV.

1. The soil and subsoil are enriched in moisture not only by atmospheric precipitation (rain, snow, fog, hail, etc.), but also by the water vapor of the atmosphere and the condensation of the water vapor moving from the lower depths toward the surface of the soil.

2. The enrichment of the soil moisture due to the water vapor of the atmosphere takes place by (a) molecular and (b) thermal condensation of the atmospheric vapor in the surface layers of the soil exclusively.

3. At 0°C. water exists in the soil in four conditions, viz., in the form of vapor, as hygroscopic meter, in a condition of films[2] and as gravitational water.

4. Hygroscopic, film and gravitational moisture are characterized by different elasticities of the water vapors and different modes of movement. (A) If the moisture is in the film or gravitational state, then the soil air, independent of the degree of saturation and temperature of the soil, has, in the first place, a maximum elasticity of water vapor for the given temperature (the relative humidity being 100 per cent). (B) In the case of hygroscopic soil moisture, the elasticity of the water vapors of the soil air does not reach the maximum saturation (relative humidity being less than 100 per cent) and depends both

[2] The author uses the Russian term "plenotchnaya" and the true translation is film. The author does not mention capillary water. His term, however, may include this.—J. S. J.

upon the degree of saturation and on the temperature of the soil, diminishing at constant temperature with a decrease of the soil moisture, and increasing at constant soil moisture with an increase in temperature. (C) Hygroscopic water may move about in the soil only upon changing into a vapor state. (D) Film water moves in the soil in a liquid condition from places of a higher moisture content to those of lower. Gravity does not influence the speed of movement of the film moisture. (E) Gravitational waters move in the soil in a liquid condition, under the influence of gravity. (F) Film and gravitational waters move about in the soil also in the condition of vapor, at a uniform moisture content throughout the soil the movement takes place from areas of higher temperature to those of lower; at the same temperature, the vapor moves from layers of higher moisture content to those of lower.

5. It is necessary to distinguish daily and seasonal changes in the distribution of the vapor pressure in soils and sub-soils. As a result of the daily changes we have (a) loss of soil moisture by evaporation and (b) the movement of water in a vapor state from the upper soil strata to the lower strata and *vice versa* are a result of the daily changes. The decrease in the intensity of these processes may be attained in agricultural technic by means of surface mulching of the soil.

6. The water with which the soil is enriched as a result of molecular condensation (see paragraph 2) of the atmospheric vapor, in connection with what has been said in paragraph 5b, is a source of water physiologically useful to plants.

7. As a result of the seasonal distribution of the vapor pressure of the moisture in the soil and subsoil we have: (a) the movement of water, in a vapor state, during the winter period, from the subsoil to the surface; this increases the moisture content of the soil, which is in turn dependent upon precipitation during the fall-winter period; (b) the movement of water from the soil and the upper layers of the subsoil into the deeper subsoil, to strata with constant yearly temperature (summer period).

8. In the stratum having a constant yearly temperature during the summer period, the formation of liquid waters should take place at the expense of the water vapor, which moves toward this stratum from below and from above. These waters may feed the subsoil waters of the first horizon fully or partly depending upon the climatic and geologic peculiarities of the regions.

9. Below the stratum where constant temperature begins the elasticity of the water vapors of the subsoil remains at times unchanged (seasonal), increasing with depth. Due to this, there is a constant one-sided movement of the water vapor from the deeper layers of the earth's crust to the less deeper strata of the subsoil. In those places where the thermal gradient increases abruptly, there should be noticed the formation of liquid waters. These waters participate in the formation of subsoil waters of the second and third horizons and so on; whereby these horizons are probably often formed in the manner indicated.

10. The moisture-holding capacity of the subsoil, which has a homogeneous structure and considerable strength, varies at different heights.

11. If the strength of a homogeneous subsoil is great enough then its upper strata possess a moisture content corresponding to the "maximum molecular moisture-holding capacity" of the given rock species; on the other hand the moisture-holding capacity of the lower strata may be considerably higher than the above unit, at times even several times as high as in the case of sand, for example; although even in this case it does not reach the full moisture-holding capacity; the moisture-holding capacity of the intermediary strata of the subsoil changes constantly, diminishing from the lower to the higher strata.

12. In a homogeneous subsoil, the moisture content of which is not higher than the maximum molecular moisture-holding capacity, the hydrostatic pressure, caused by additional moistening of the subsoil, is not transmitted through strata with a moisture content described above.

13. In a homogeneous subsoil, the moisture content of which is greater than the moisture corresponding to the maximum molecular moisture-holding capacity, hydrostatic pressure is transmitted from some strata of the subsoil to others.

14. In homogeneous subsoils of great strength with an established equilibrium of water, an additional moistening of the upper strata calls forth a movement of a similar amount of water into the strata of the subsoils. This translocation is accomplished in the following manner: while the newly added water moves along the strata with a moisture content corresponding to the maximum molecular moisture-holding capacity, the equilibrium of the water in the lower strata of the subsoil is not disturbed (paragraph 12), and the water of the lower horizon of the subsoil does not leach out; however, equilibrium is disturbed as soon as the newly added water reaches the horizon with a moisture content greater than in a strata with a maximum molecular moisture-holding capacity, (paragraph 13); then during a certain period of time, the length of which is determined by the rapidity of transmission of the hydrostatic pressure in the given rock species, leaching of water from the lowest strata of the subsoil takes place.

15. Observations on the moisture content of the subsoils in nature show, in connection with the depth of the water table, amount of precipitation and energy of evaporation of water by plants and soil, that in northern regions the penetration of the precipitated waters up to the first horizon of the water table seems to take place during the greater part of the year. In the southern regions, the penetration of the precipitation adapts itself to a shorter period, the end of winter and beginning of spring. In the deserts with clay soils and subsoils, we may assume with sufficient probability of absence of the penetration of the precipitation to the first horizon of the water table.

16. In the low parts of the relief, the penetration of the precipitation to the first horizon of the ground waters may take place in all widths (in a horizontal plane?).

17. In the regions of sandy and fine sandy soils and subsoils, the penetration of the precipitation may reach the first horizon of the ground waters, independent of the location of the region, for the maximum molecular moisture-holding capacity of such soils is very small and the penetration of the water in such soils takes place relatively fast.

18. In soils which are not of a homogeneous character, the waters are distributed at equilibrium in a different manner than in the soils of homogeneous structure (paragraph 11); however, this does not change the conditions established in paragraphs 12, 13, 14.

19. The penetration of precipitation apparently is possible down to second and third horizons of the ground waters and so on, if the layer of the ground waters possesses some penetrability and the hydrostatic pressure of the ground water is sufficiently great to overcome the forces of resistance, which develop with the movement of the water both in the impervious layer as well as at the contact points with the underlying strata.

20. The ground waters are formed both by condensation of the water vapor of the soil, subsoil and juvenile waters, and also by the infiltration of the liquid waters (precipitation, ground waters of the overlying horizons.) Apparently it happens more often that these processes take place simultaneously, superimposing one another. However, there are in nature undoubtedly also such conditions when the ground waters are formed by condensation exclusively. In either case the ground waters must find themselves on a relatively pervious layer. In the latter case the condition of the ground water may not correspond with the condensation layer, where liquid water is formed from water vapor.

Origin of Alkali Soils. D. G. VILENSKY.

1. All salinized soils begin with the salines (solontshaki) which originate in the zones where the evaporation is greater than the atmospheric precipitation; in places where the water table is raised to the surface, as a result of which the capillary rise brings up water-soluble mineral salts and concentrates them at the surface. The sources of the salts are either the parent rocks, if they contain salts, or the ground waters if they contain in solution mineral substances.

2. The alkali soils differ from normal soils not only by the presence of large amounts of salts, but also by the properties of the zeolitic portion. When sodium salts enter the soil an absorption of sodium, by the zeolitic substances takes place, and if such a soil loses its salts it will not return again to its original condition, for its zeolitic (and humic) portions will contain even after the removal of the excess of sodium salts from the soil solution, certain amounts of zeolitic sodium.

3. All the above groups of soils containing salts represent the product of metamorphosis of salines and originate from them after the contact with the ground waters, which feed them, ceases. The washing of the salines by atmospheric precipitation as well as the removal of the salts from the surface horizons into the lower depths takes place first, then the alkalization of the surface

begins, due to the formation of sodium carbonate as a result of washing. According to Gedroitz, this sodium carbonate is formed at the expense of the zeolitic sodium as a result of double exchange of calcium carbonate and the zeolitic portion. After the electrolytes are washed out and the formation of sodium carbonate has begun, the semi-reversible colloids of the soil change into sols and, by passing downward they clog up the capillaries and create at the surface of the soil conditions of temporary excess of moisture; these conditions are among the main causes of the continuance of the metamorphosis of these soils.

4. In the post tertiary valleys of Eurasia (European Russia), the saline soils which later gave rise to alkali soils were formed during the dry postglacial epoch when the dry and warm climate and the prevalence of lakes, high level of river waters and ground waters favored the formation of local accumulations of water soluble mineral salts in the upper layers of the subsoils. Thus the alkali soils are a derelict formation chiefly of the postglacial epoch. This does not exclude their possible formation in our times, especially at the outcrops of parent rocks containing salts.

5. Those groups of alkali soils which we may observe now represent separate stages of a process of gradual metamorphosis of salines, under conditions of various climatic zones. The geographic regularity of their distribution in the valleys of Eurasia indicates the direction of this metamorphosis.

6. In our present geologic epoch, in the zones of the dry steppes, the tshernoziems, forest steppes, and finally in the forest zone, an active process of a gradual decomposition of the soils containing salts is going on under the combined influences of the waters standing on their surface, the accumulations of meadow and marsh vegetation, and the oncoming forest. The final result of all these factors is the conversion of alkali soils into degraded soils, which, in their outer appearance, resemble the podzols of the forest zone.

On the Amelioration of Salinized Soils. D. G. VILENSKY.

1. Notwithstanding the great number of theoretical investigations and practical experiments conducted largely in the United States, the problem of amelioration of soils containing salts cannot be considered as solved even in its first stages. This is due chiefly to the fact that there is no satisfactory understanding of the origin of such soils.

2. The new theory of the origin of alkali soils makes it possible to draw several conclusions which are interesting from the standpoint of amelioration of soils containing salts. From the standpoint of this theory, one of the main routes to the solution of this problem is the study of the process of degradation of alkali soils and the great experiment of the destruction of these soils which nature itself has performed in our present epoch.

3. Measures of radical amelioration of alkali soils without irrigation, known at the present time are mechanical removal of the structural horizon; the addition to the alkali soils, in the process of their cultivation, of manure, peat,

leaves, marsh and acid meadow soil, probably certain mineral fertilizers of an acid reaction, as superphosphates, and lastly, green manuring. These measures are directed towards enrichment of the alkali soils with organic materials which are to undergo decomposition at times of excessive moisture.

4. The measures which may be taken to prevent the formation of saline soils under irrigation are: preventing the rise of the water table; leaching the salines with the purpose of lowering in them the concentration of easily soluble salts; regular measures to counteract the harmful effects of leaching such as an increased basicity and extremely undesirable physical properties. The planting of appropriate shade trees and shrubs along irrigation canals may be recommended for shading the soil and tending to preventing the rise of underground waters.

The Absorbing Power of Soils and the Principle of Automatic Self-Irrigation of Soils. B. G. KORNEV.

Soils possess the ability to absorb water with a certain power. Until now, the nature and power of this property has not been studied. In the spring of 1921 the author constructed an apparatus which measures this power with a mercury manometer. The work with this apparatus in measuring the absorbing power made it possible to establish the following:

The absorbing power of the soil is free energy which may be utilized for irrigation purposes. In the main, the system of automatic irrigation (used by the author) consists in the following:

1. The absorbing power of soils varies with different soils depending on structure, degree of compactness, size of the mechanical particles of the soil and degree of soil moisture. Thus the absorbing powers of the soils studied were expressed by the following manometer readings: heavy compacted loam, 51 cm.; non-compacted loam, 46 cm.; fine compacted sand, 40 cm.; fine non-compacted sand, 33 cm.

2. The absorbing power of soils varies inversely with the degree of soil moisture. At optimum moisture, the power of absorption practically ceases, and at full moisture-holding capacity approaches 0.0 cm. Thus, for instance, for a heavy loam:

Moisture:	2%	16%	23%	27%	32%	40%
Absorbing power:	51 cm.	24 cm.	16 cm.	10 cm.	0.5 cm.	0 cm.

and for a fine sand:

Moisture:	2%	7.6%	13%	16.3%	28%
Absorbing power:	30 cm.	17 cm.	10 cm.	3 cm.	0 cm.

3. The apparatus used may serve as a standard for the measurement of the soil moisture.

4. The absorbing power of the soil is a surface energy phenomenon of the soil particles.

5. The optimum content of soil moisture is a constant unit for each soil corresponding to the moment of change of film water into liquid drops.

Special porous tubes are placed in the soil. They are united into one closed net work and are filled with water. The walls of the tubes become saturated with the water. The soil, due to its power of absorption, begins to absorb the water from the tubes and becomes moist. As a result, a change in pressure takes place, and water from the lower lying reservoir rises through the main tube of the system and makes up the loss. The height to which the water

rises may reach six to seven meters. When the soil is saturated with water the absorbing power falls and the income of water ceases; in the case of over-saturation, the excess of water goes back through the pipes into the reservoir and the irrigation system works like a drainage system. A constant definite per cent of moisture may be established by this method of irrigation, as the soil itself serves as a regulator.

Following the principle of utilization of the soil's absorbing power for irrigation purposes, pot experiments were started with an automatic self-irrigating system. The vessels consisted of two pots, an inner porous pot and an outer impervious pot. The water is placed between the two pots; when the soil is placed in the inner pot, the water is absorbed by the soil through the walls of the porous pot and becomes moist; a lowered pressure results within the vessel as a result of which the water from a feeding reservoir flows automatically towards the space between the two vessels, making up the loss. A whole series of such vessels may be thus arranged with one reservoir, and the soil is then moistened automatically. By lowering the water level in the reservoir, the percentage of moisture may be changed in the pots.

The Root System of Grasses in Soils of the Podzol Type. G. A. KATSHINSKY.

On soils of the podzol type, the grasses develop the chief mass (about 90 per cent) of large and small roots in the plowed horizon. The podzol under-horizon, unproductive in composition and unfavorable on account of its physical properties, serves as a hindrance for root development which is hard to overcome. In the compact underhorizon which is alluvial, the roots penetrate along the crevices and worm borings, not forcing independent paths through the soil. The soil in such cases presses on the roots.

The Characterization of the Main Soil Types from Data of Absorbed Bases. V. V. HEMMERLING.

A clear understanding of soil-forming processes cannot be gotten simply by a study of the morphology of soils. The searching of the paths of this process should be chiefly a static study. A total analysis or extractions with hydrochloric acid do not give a satisfactory characterization of a soil. The absorbed bases—the most mobile and active part of the soil—which are present either in solid or liquid phase, may give well defined data for the determination of the genesis and broad characterization of soil types. The author illustrated his paper with a large series of charts, which characterized the various soil types according to the content and distribution of the absorbed bases.

The Differentiation of Podzol Soils by Morphological Indices. A. A. KRASIUK.

The following indices were presented by the author as a basis for identification of podzol soils.

1. The absence of a moist immobile atmosphere over the soils indicate good insulation [*literal translation*—ED.]

2. Gray or dark gray color of the rocks. A tensile strength not less than 14 cm.

3. Slightly granular, lumpy, nut-like structure of the rocks. Traces of digging animals.

4. Weak podzolization or slight loss of bases of the rocks. The stratified structure is not clearly expressed.

5. Medium loam as a subsoil; porous and with a large nut like or prism-like structure.

6. Presence of carbonates.

7. Absence of sharply expressed ortstein or alluvial horizon and the presence of a moderate quantity of boulders.

8. Apparent, gradual, and wide sloping. Peculiarities of exposure: slightly rolling relief or slightly sloping water sheds.

9. Absence of sharp coloration of the plow zone.

On the basis of these indices, the podzol soils were classified according to their productiveness into ten groups.

GERMANY[3]

The papers discussed in this section have all appeared since the publication of the fourth edition of Bodenkunde für Land- und Forstwirte, 1923.

Investigations in Soil Physics

The work done by Ferd. Zunker and G. Krauss concerns soil structure (Landwirtschaftliche Jahrbücher, v. 58, p. 159–203; and Internationale Mitteilungen für Bodenkunde, v. 13, p. 222.) Both investigators use Wiegner's method for the determination of the suspension curve which represents the sedimentation of soils suspensions per time unit. From these data they try to find the total soil area. In the most recent work of Johannes Rothe (Landwirtschaftliche Jahrbücher) it is, however, pointed out that this is impossible notwithstanding Zunker's ingenious calculations. This is obvious because the fundamentals of the suspension analyses cannot be considered to be satisfactory for this purpose. A paper from G. Hager deals with the changes in soil structure, which he thinks are caused by colloid-chemical phenomena. (Zeitschrift für Pflanzenernährung und Düngung, part A, v. 2, p. 292–311.)

Hans Göttsch (Dissertation, Kiel, 1922). Georg Ruhnau (Dissertation, Königsberg, 1922), and Bernhard Szonn (Dissertation, Königsberg, 1923) studied the behavior of the soil to water.

Göttsch found that the ascent of water in vertical tubs can be represented by the following equation:

$$t = \frac{8n}{r^2 g}\left(2.302\, h \cdot \log \frac{h}{h-x} - x\right)$$

In this equation h = height of ascent
x = momentary height of ascent during time $\backsim$
g = gravity
n = coefficient of internal friction
(coefficient for water at 15°C. = 0.0115
2.302 = modulus
r = radius

Göttsch remarks that in experiments performed by Von Seelhorst the soil water did not rise to the surface by capillary action. Soil cultivation did not influence the water evaporation, the latter being the same for compact and non-compact soils. This was true for his own experiments as well as for Von Seelhorst's.

Ruhnau studied the relation of sandy soils of different fineness to water. The size of the particles was found by determining weight and specific gravity of a great number of them. He worked chiefly with a quarry sand and a sea sand and determined water capacity, water permeability, water ascent and water evaporation in these sands.

Szonn determined the size of the particles in the same way and found the following relationship between the water permeability and the size of the particles:

For a sea sand: $\log (33.36 - y) = \log 33.36 - 5.3x$
For a quarry sand: $\log (39.85 - y) = \log 39.85 - 4.3x$
x = size of particles in cubic centimeters
y = required quantity of water in cc. per minute per square centimeter of filtration surface

The differences in the constants are due to the different shapes of the particles.

Szonn mixed the soil with varying amounts of sand (with a maximum of 80 per cent sand) and found that the required quantities of water (x) increased with the percentage (y) sand in the soil, in the following way:

For a loam soil: $\log (80 - y) = \log 80 - 1.5 (x - 0.20)$
For a peat soil: $\log (80 - y) = \log 80 - 1.5 (x + 0.58)$

A splendid contribution to the knowledge of soil cultivation has been given by Otto Born (Inaugural Dissertation, Königsberg, 1923). He improved Von Schermbeek's soil probe by supplying a device registering the energy produced. He determined the energy required for different soil types as a function of the water content and also as a function of the air space in the soil.

Investigations in Soil Chemistry

Engels (Zeitschrift für Pflanzenernährung und Düngung, part B, v. 2, p. 185–209) gives us a general study on the solubility of soil plant food in relation to fertilization.

J. König, J. Häsenbaumer, and J. Schäfer (Landwirtschaftliche Jahrbücher, v. 58, p. 55–124) try to find the relationship between the plant food present in the soil and the food taken from it by potatoes. They state that 1 kgm. of normal potatoes should contain 25 gm. of potassium, 18 gm. of nitrogen and 6 gm. of phosphoric acid. An abundance of these foods in the soil is indicated if the potatoes grown upon it contain larger amounts of these elements while the soil is considered deficient if lower amounts are found in the potato crop. Such data will permit only a rough estimate because, according to the results obtained by the reviewer, the food taken up by the crop depends not only upon the plant-food contained in the soil but also on other factors determining the total yield. More attention has been paid to these facts in a later publication by J. König and J. Hasenbäumer entitled "Die Ermittelung des Nährstoffbedarfes der Pflanzen und des aufnehmbaren (ausnutzungsfähigen) Nährstoffvorrats im Boden" (Landwirtschaftliche Jahrbücher, v. 59, p. 97–126).

Eilh. Alfred Mitscherlich shows in his paper "Der Düngungsversuch" (Landwirtschaftliche Jahrbücher, v. 58, p. 125–158) how the records obtained from fertilizer experiments in the field can be made to agree with pot experiments. He suggests a method for transforming the records of pot experiments for field use. In a second paper he shows how it is possible to determine by means of pot experiments, the quantity of available plant food present in 100 gm. of soil (Landwirtschaftliche Jahrbucher, v. 58, p. 601–617). The law of the growth factors as established by the writer is the fundamental principle for these studies. In a third paper, prepared in coöperation with H. Wagner, the increase of yield caused by increasing applications of potassium and magnesium was studied (Landwirtschaftliche Jahrbücher, v. 58, p. 645–652). The investigators who used sand cultures for their experiments state that magnesium causes an increase in yield only where there is a real lack of magnesium in the soil. A favorable side effect (Nebenwirkung) could not be observed under these conditions.

Still further objection is made by O. Lemmermann and Paul Ehrenberg against the system of Aereboe-Wrangell which was proposed for the purpose of saving phosphoric acid. The question of reaction in connection with phosphoric acid fertilizers is also discussed extensively (Zeitschrift für Pfanzenernährung und Düngung, part B, v. 2, p. 73–91, 129–136, 408–423).

Münter reports on the influence of alkaline soil reaction on production (Zeitschrift für Pflanzenernährung und Dungung, part B, v. 2, p. 289–298). He shows that the application of the stronger alkaline fertilizers does not do as much harm to heavy as to light soils. A loam soil should not contain more than 0.35 gm. soluble alkali per kilogram, while this amount should not exceed 0.20 gm. in the case of a sandy soil. The sensitiveness of different plants may differ very much.

Gering and Sander showed in their study on soil acidity (Zeitschrift für Pflanzenernährung und Düngung, part B, v. 2, p. 299–314) that the action of the acidity differs very much for different plants. Even the same acidity may

influence the same crop in different ways. Therefore, great care should be taken in judging the relationship between soil acidity and plant growth.

Further investigations on the influence of carbon dioxide on plant growth were made by Paul Spirgatis, who showed that an increase of the carbon dioxide content of the air could give an increase in yield only if the light factor were depressed (Botanisches Archiv. Verlag des Repertoriums, Dahlem bei Berlin, v. 4, p. 381–403, Inaugural Dissertation, Königsberg i. Pr. 1923).

A. Densch and Th. Hunnius (Zeitschrift für Pflanzenernährung und Düngung, part B, v. 2, p. 241–252) studied the action of increased carbon-dioxide supply in the field. An increase in yield due to carbon dioxide was not observed.

Otto Lemmermann (Zeitschrift für Pflanzenernährung and Düngung, part B, v. 2, p. 142–146) experimented with rye using different quantities of seed per unit and fertilizing in different ways. The records obtained in the different years were not the same.

THE NETHERLANDS[4]

Investigations on Nitrification and Denitrification in Tropical Soils. F. C. GERRETSEN. Archief Suikerindustrie Nederlandsch Indie 1921, vol. 29, pp. 1397–1530.

The primary purpose of this investigation was to study the relation existing between the fertility of several sugar cane soils and rice soils and the nitrification and denitrification in these soils. It was shown that important differences can exist in the nitrifying power, while these differences do not influence the general appearance of the sugar cane. The crops appeared poor without any exception when denitrification took place in the natural soil to which only nitrate was added. Extracts were obtained from a number of infertile soils in which the nitrification was delayed for several weeks. This was caused by toxic substances which disappeared when the soil was thoroughly aerated.

These substances could also be removed from the extracts by shaking with a well aerated soil. As a rule, poor nitrification is found in good rice soils on account of their wetness. A considerable amount of nitrate-nitrogen, which remains in the soil after the sugar cane has been harvested, is lost every year through denitrification in the wet sands. Nitrite formation after fertilizing with ammonium sulfate seemed to depend on the hydrogen ion concentration. Nitrate formation was not detectable when the reaction was more acid than pH 7.2, nitrate formation then going on faster than nitrite formation. A typical reduction of iron compounds shows itself in soils which have been submerged for some time. In "sawahs" this is indicated by the presence of a blue color which disappears again when the soil is aerated. FeS was not present in these soils. A measure of the aeration appeared to be the proportion of the amount of iodine which were liberated from an acidified solution of potassium iodide by the same soil before and after aeration.

On the Occurrence of a Bacteriophage in the Nodules of the Leguminous Plants. F. C. GERRETSEN, A. GRYNS, J. SACK, AND N. L. SÖHNGEN. Centralblatt für Bacteriologie, Part 2, v. 60, P. 311.

Bacteriophage were isolated from the nodules of clover, lupines and serradella and were also obtained from the stalks and roots of these plants. Possibly this might give an explanation for the way in which the bacteria are dissolved in the nodules. The lytic action is very specific, e.g., the serradella bacteriophage does not dissolve the bacteria of the lupines. Bacteriophage could be isolated directly from farm and garden soil, but they could not be obtained either from heather or forest soil. The resistance of the bacteriophage to the rays of ultraviolet light is at least eight times as great as for the bacteria concerned.

Report on the Investigation on the Causes of the Poor Appearance of Some Crops in Zeeland. D. J. HISSINK AND K. ZYLSTRA. Verslagen van Landbouwkundige Onderzoekïngen der Rykslandbouw Proefstations (Reports on the agricultural research work of the State Agricultural Experiment Stations), 1922, no. 27, p. 1–12.

The poor appearance of some crops (beets and alfalfa) during the abnormally dry summer of 1921 was considered to be due to inadequate water supply to the bad spots of the surface soil, especially where sandy layers occurred near the surface.

Studies on Samples of Soil and Dredged Mud from the Polders and Lakes East of the Utrechtse Vecht in Connections with the Draining Plans of These Lakes. DR. D. J. HISSINK. Internationale Mitteilunger für Bodenkunde, v. 11, p. 166–183.

This is a contribution to the knowledge of the chemical composition of bottom peat soils.

The Black Clay of Thesinge (in the province of Groningen Holland). CHR. BROCKMANN AND D. J. HISSINK. Verhandelingen van het Geologisch-Mynbounkundig Genootschap voor Nederland en Kolonien, geologische serie, v. 6, p. 43–55.

The black clay lies on the top of alluvial North Sea clay; for this reason it cannot be potters' clay (Launenburger Ton von Schucht) though it resembles the latter strongly. It differs from potters' clay, however, by its content of diatoms and other organic residues.

A Simple and Quick Method for Determining Soil Acidity. D. J. HISSINK. Chemisch Weekblad (1922), v. 19, p. 281–283.

The method Comber used for recognition of acid soils (treatment of 2 gm. of air-dry soil with 5 cc. of a 4 per cent solution of KCNS in 95–96 per cent alcohol) was applied to a great number of different soil types; the pH value of an aqueous suspension of these soils had been determined with the potentiom-

eter. These comparative determinations showed that a satisfactory relation existed between the potentiometrical pH value and the red color obtained by shaking Comber's reagent with the air-dry soil. In most cases, sufficient accuracy was obtained when the soil acidity was estimated by the red tint. Simple instruments and a color chart have been placed at the disposal of the farmers.

Some General Conceptions on Acidity and the Rôle Played by It in Several Processes. DR. D. J. HISSINK. Verslagen van Landbouwkundige Onderzoekingen der Rykslandbouw Proefstations (1922), no. 27, p. 133–145.

An understanding of soil acidity and its probable influence on plant growth can be had only when the acidity of a solution is defined in scientific terms, when it is known how the acidity is expressed by figures and which factors influence it. This article tries to explain these facts to well trained farmers.

The Acidity of the Soil. D. J. HISSINK AND JAC. VAN DER SPEK. Verslagen van Landbouwkundige Onderzoekingen der Rykslandbouw Proefstations (1922), no. 27, p. 146–161.

This paper consists of six sections as follows:

1. The components of the soil affecting soil acidity, namely, carbon dioxide, calcium carbonate, clay and humus substances. It is argued that the acidity of an aqueous soil suspension is determined by the number of adsorptively bound hydrogen ions present in the outside layer of the electric double layer surrounding the particles. Therefore, this acidity will depend upon the saturation condition and upon the extent to which the soil acids are dissociated (clay acids and humus acids).

2. Investigations on the acidity of Dutch soils: The pH value of the aqueous soil suspensions were determined potentiometrically. Soils containing calcium carbonate were faintly alkaline with an average reaction of about pH 7.5. The reaction of the humus soils (bottom peat soil, upland peat soil, humus clay soil, humus sandy soil) was between pH 3.5–4.0 and pH 8. The reaction of the clay soils with little or no humus was between pH 6.0 and pH 8.0. There was a relationship between the hydrogen-ion concentration and the lime content calculated of the clay and humus.

3. Relationship between soil acidity and plant growth: It is claimed that the need of lime is closely related to the optimum acidity for any given soil and for any given crop.

4. The changes in soil acidity: The changes in the pH values due to the influence of different salts are discussed and explained.

If, for instance, a soil is treated with a solution of potassium chloride the K ions are exchanged not only for Ca, Mg and Na ions, but also for the adsorptively bound hydrogen ions of the soil.

$$\text{Soil-H} + \text{KCl} \rightleftarrows \text{Soil-K} + \text{HCl}$$

Through this reaction the acidity of the solution will increase and the soil acidity will decrease. The acid solution acts on the compounds of aluminum and iron in the soil, dissolving relatively large amounts if its strength is sufficient. When the soil is treated with solutions of salts derived from weak acids, e.g., potassium acetate, the equilibrium

$$\text{Soil H} + \text{KAc} \rightleftarrows \text{Soil}-\text{K} + \text{HAc}$$
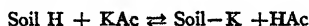
will be moved far to the right in consequence of the slight dissociation of the acetic acid. The pH value changes only slightly, but when the filtrate is titrated with alkali rather high titration figures can be obtained. If a soil is treated with a solution of potassium chloride the real acidity (hydrogen-ion concentration) is greater and the titration figure (number of cubic centimeters of alkali needed for neutralization) is smaller than when the same soil is treated with a solution of potassium acetate. For figures concerning these investigations the reader is referred to the next abstract.

5. Relationship between the saturation point and soil acidity. This relationship is observed for a collection of clay humus soils.

6. Buffer condition and buffer value of the soil. The conception of buffer condition is generally discussed and explained.

The Action of Solutions of Neutral Salts on Soil. A Contribution to the Knowledge of Soil Acidity. JAC. VAN DER SPEK. Verslagen van Landbouwkundige Onderzoekingen der Rykslandbouw Proefstations (1922), no. 27, p. 162–202.

In the first section a review is given of the prevailing opinions on the action of solutions of neutral salts on soils, resulting in an acid reaction of these solutions. In the second section the apparatus of the hydrogen electrode is discussed and also the way in which the pH values of the soil suspensions are determined by this device. Section 3 contains the results of the action of a 10 per cent solution of potassium chloride on about twenty soils of different types. The pH values found for the aqueous suspensions and for the KCl suspensions of these soils showed that all KCl suspensions of the acid, neutral and alkaline soils were more acid than the aqueous suspensions. Therefore all soils treated with the KCl suspensions of the most acid soils contained detectable quantities of aluminum and iron.

In view of these results it must be concluded that the colloidal particles of clay and humus of all soils contain adsorptively bound hydrogen ions as well as the adsorptively bound Ca, Mg, K, and Na ions. These adsorptively bound hydrogen ions can be replaced by other cations. When a soil is treated with a solution of a neutral salt such as potassium chloride a chemical reaction must take place between the adsorptively bound ions of the soil (Ca, Mg, K, Na and H) and the free ions of the solution. This reaction may be represented by the following equilibrium equation:

$$\text{Soil} \begin{cases} \text{Ca} \\ \text{H} \end{cases} + \text{K} + \text{Cl} \rightleftarrows \text{Soil} \begin{cases} \text{Ca} \\ \text{K} \\ \text{H} \end{cases} + \text{K} + \text{Cl} + \text{Ca} + \text{Cl} + \text{H} + \text{Cl}$$
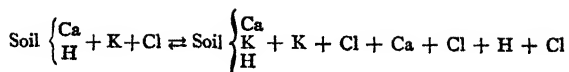
In this equation, Mg, K, or Na may be substituted for Ca. From this equation it can be concluded that the quantity of cations exchanged is influenced by the concentration of the salt solution used.

This has indeed been observed as a fact by several investigators, (Way, Aberson, and Harris among others) who found also that this exchange takes place according to the adsorption isotherm as the concentrations of a salt solution increase. It is observed, moreover, that the process of exchanging cations is not only influenced by the concentration of the salt solution used, but also depends on the kind of salt used for the solution. This was especially studied for KCl, KCNS, K_2SO_4, CH_3COOK and $CaCl_2$. The results obtained with these salts could be interpreted by the equation given above. It is further pointed out that the phenomena observed, when soils are treated with solutions of neutral salts can indicate a chemical reaction (the exchange of equivalent quantities of the cations Ca, Mg, K, Na, and H; the progress of reaction in case a more or less dissociated substance is formed) or an adsorption phenomenon (the equilibrium is represented by the adsorption isotherm; the action of the different salts with the same kation or anion). It is undoubtedly a fact that a reaction takes place between the free ions of the solution and the adsorptively bound ions of the soil. On account of these facts the opinions existing about the action of neutral salts on soils could be made to agree, if adsorption phenomena were considered to be chemical reactions between the free ions the adsorptively bound ions. In this case the expression "adsorptively bound" should be understood to refer to ions situated on the surface of colloidal particles, practically not washed out by water, but exchangeable for other ions of the same electric charge. In section 4, Kappen's extended investigations on soil acidity are discussed also in connection with the theory developed on the action of salt solution on the soil. Section 5 deals with the formation of adsorptively bound hydrogen ions in the soil; and section 6, with the claims that the colloidal clay and humus particles contain adsorptively bound hydrogen ions.

The Influence of Acid and Alkaline Fertilizers on the Growth of Crops. (*Six Years of Practical Experience on the Plots of Spitsberger.*) J. HUDIG AND C. MEYER. Verslagen Landbouwkundige Onderzoekingen Rykslandbouw Proefstations (1922), no. 26, p. 60–68.

The conclusions drawn by these authors are:

1. Acid fertilizers should not be applied on acid soils (except for potatoes).

2. Leguminous plants either do not grow on acid soils or their growth is insufficient. They demand slightly alkaline or neutral soils.

3. Potatoes require a slightly acid soil.

4. It can be determined by means of laboratory research whether a soil requires a dressing of lime for neutralization or not; and if lime is required, the quantity needed.

The Potato Scab in Its Relation to Climate and Soil. H. M. QAUNJER AND J.
  HUDIG. Cultura, Jaargang 35 (1923), p. 1–12.
A relationship was observed between soil acidity (pH value) and the scabby
character of potatoes. The scab occurred on slightly acid and on alkaline
soils. No scab, or only a very slight amount of scab was observed on soils with
pH values of 5.5–5.0 or less. The dry year of 1921 proved to be a very severe
scab year.

Soil Water Level, Capillarity and Evaporation. J. F. LICHTENBERG. Cultura,
  Jahrgang 34 (1922), p. 262–270.
The writer points out the great importance of understanding the relation
between the movement of soil water and the draining of the Dutch polders.
The necessity of studies in the line of soil physics is emphasized.

*The Influence of Soil Type and Fertilization on the Nitrogen and Ash Contents
  of Our Farm Crops.* J. G. MASCHHAUPT. Verslagen van Landbouwkundige
  Onderzoekingen der Rykslandbouw Proefstations, no. 27 (1922), 10th com-
  munication, no. 28 (1923), 11th and 12th communication.
The replacement of potash by sodium is discussed in connection with infor-
mation given about mangolds. It is shown that potassium and sodium, and
calcium to a less extent, can partially replace one another in equivalent
quantities.

THE EFFECT OF SEVERAL MINERAL FERTILIZERS UPON THE NODULATION OF VIRGINIA SOY BEANS[1]

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Among the outstanding data on the effect of mineral fertilizers upon the nodule-forming organisms and their symbiotic relationship with legumes are those of Prucha (6), Wilson (4), Fellers (2), and Heinze (5). Prucha found that elements essential for plant growth greatly increased nodulation when applied in small amounts. Wilson observed that an application of these elements would aid the symbiotic relationship. Fellers found that under many conditions nodulation was increased by an application of phosphorus, calcium, or potassium. Heinze found that the addition of phosphorus or potassium to a soil had little if any effect upon its content of symbiotic nitrogen fixing organisms. The author concluded after a review of the literature and in consideration of some data collected in 1920–1921 (experiment 1 of this paper) that elements essential for plant growth have little, if any direct effect upon the infection and nodulation of leguminous crops. The work reported in this paper was outlined to determine what effect the essential elements would have upon nodulation when the unknown factors were reduced to a minimum and all known factors controlled as far as possible.

SCOPE

This paper reports a study of the effect upon nodulation of the four essential elements most likely to be limiting factors. These elements were applied as calcium carbonate, potassium chloride, sodium nitrate, and acid phosphate; except in experiment 1 where sodium phosphate was used. All conditions were controlled as much as possible under green house conditions. Experiment 1 is a study of the effect upon nodulation of calcium, potassium, and phosphorus when they were applied according to the triangle plan as frequently used by Schreiner and others. Experiments 2–5 are studies of the effect upon

nodulation of increasing applications of phosphate, potassium, calcium,and nitrate respectively. Several different substrata were used and they were maintained at different degrees of saturation.

METHODS

Wherever possible standard methods were employed.

Inoculation was always accomplished by mixing the emulsions obtained from the growth upon agar slants of three separate strains of *Bacillus radicicola*. The emulsions were obtained by scraping the growth free from the agar with a platinum needle, shaking vigorously with a small quantity of sand and then transfering aliquot parts to the several pots. Care was always taken to add a sufficiently large number of organisms to insure that maximum nodulation would not be prevented by a lack of the infecting organisms. By using three strains of the organism the presence of a viable culture has been more definitely assured.

After washing the white quartz sand used, it was exposed to the sunlight until air-dried to assure the absence of nodular organisms.

A uniform plant stand was obtained by sowing twenty seeds to the pot and thinning the resulting seedlings to ten per pot.

Application of fertilizers was made whenever possible by means of solution and aliquot parts. With insoluble materials, the fertilizer was usually weighed out for each application.

Hydrogen-ion determinations were made colorometrically according to the method outlined by Gillespie (4). Generally the determinations were made on only one of duplicate pots.

The water-holding capacity of the various substrata was determined by the use of Hilgard cups.

The chemical methods employed in determining the soluble material in the various substrata were in general the methods of the Association of Official Agricultural Chemists (1). In a few cases other methods were used.

The harvests were made at the end of four weeks of growth.

Nodular counts were made after freeing the roots of the host from the substratum by gently washing them in water.

The mechanical determinations were made according to the method of the United States Bureau of Soils (3).

EXPERIMENT 1. RELATIVE NODULATION FROM TREATMENT IN ACCORDANCE WITH THE, "TRIANGLE PLAN"

In attempting to determine the fertilizing mixture which would be most favorable to the nodulation of legumes it was decided to apply several fertilizers on a triangular basis. A general survey of the literature seemed to indicate that the desired fertilizing mixture would be approached by an application of one ton per acre of a nitrogen-free fertilizer containing calcium. Accordingly the fertilizers applied were calcium carbonate, potassium chloride, and sodium phosphate. A total application of one ton per acre was made and the increments were two hundred pounds each. Each pot received also a small amount of magnesium and ferrous sulfates. By this system twenty-one pots receiving different fertilizing applications were set up. The applications made are listed in table 1. The crop was grown in three-pound pots filled with washed sand which was maintained at 75 per cent saturation by daily waterings with

distilled water. The results obtained show that when lime is absent or present in only small amounts nodulation is greatly limited. With the exception of this limitation in the absence of lime all the pots gave approximately equal nodulation. The conclusion drawn is that the salt balance has little effect on nodulation when there is a small amount of lime present. The results given are those for *Virginia* soy beans, but as other varieties of soy beans as well as

TABLE 1

Nodulation as affected by various fertilizers

POT NUMBERS	FERTILIZER FORMULA			NUMBER OF NODULES PER 10 PLANTS	WEIGHT OF AIR-DRIED TOPS PER 10 PLANTS
	$CaCO_3$	KCl	NaH_2PO_4		
	proportional parts				*gm.*
1–1	0	0	10	10	0.693
1–2	0	2	8	25	0.781
1–3	0	4	6	14	0.803
1–4	0	6	4	31	0.678
1–5	0	8	2	26	0.779
1–6	0	10	0	18	0.825
2–1	2	0	8	103	0.807
2–2	2	2	6	60	0.735
2–3	2	4	4	83	0.678
2–4	2	6	2	75	0.902
2–5	2	8	0	86	0.857
3–1	4	0	6	87	0.739
3–2	4	2	4	79	0.803
3–3	4	4	2	62	0.909
3–4	4	6	0	97	0.917
4–1	6	0	4	93	0.813
4–2	6	2	2	85	0.792
4–3	6	4	0	59	0.697
5–1	8	0	2	74	0.761
5–2	8	2	0	68	0.661
6–1	10	0	0	80	0.803

other leguminous crops gave similar results it may be assumed that the results obtained throughout the work will hold in a general way for all leguminous crops.

EXPERIMENT 2. EFFECT OF PHOSPHATE UPON NODULATION

By varying only a single fertilizer the effect of its absence or presence in excess may be determined if all other elements are present in amounts favorable to nodulation and plant growth. Acid phosphate was applied at rates vary-

ing from nothing to three thousand pounds per acre. Applications were made to three different substrata and each substratum was maintained at four different degrees of saturation. The substrata used were washed sand, sassafras

TABLE 2

Effect of increasing applications of acid phosphate upon nodulation

SATURATION OF SUBSTRATUM	ACID PHOSPHATE APPLIED PER ACRE*	REACTION OF SUBSTRATUM AFTER 2 WEEKS' GROWTH AND NUMBER OF NODULES PER TEN PLANTS AFTER 4 WEEKS' GROWTH								
		Washed sand			Penn loam			Sassafras loam		
		First	Second	pH	First	Second	pH	First	Second	pH
per cent										
	0	52	45	6.8	8	9	5.3	27	25	6.4
	50	43	40	6.7	6	8	5.5	30	10	6.6
	250	23	25	6.6	1	1	5.5	85	70	6.6
25	500	18	15	6.7	1	2	5.5	33	30	6.6
	1,000	8	8	6.4	0	0	5.5	27	25	6.6
	2,000	2	2	6.5	0	0	5.5	0	0	6.8
	3,000	0	0	6.6	0	0	5.3	27	25	6.5
	0	80	60	6.6	24	26	5.2	55	60	6.5
	50	67	60	6.7	18	20	5.5	45	50	6.6
	250	36	36	6.7	15	12	5.3	35	60	6.6
50	500	33	29	6.7	12	12	5.5	30	†	6.8
	1,000	21	20	6.5	6	5	5.7	40	†	6.5
	2,000	7	5	6.5	0	0	5.3	70	70	6.6
	3,000	0	0	6.6	0	0	5.6	10	10	6.5
	0	80	90	6.5	30	24	5.5	90	†	6.6
	50	70	60	6.8	45	50	5.4	†	†	6.8
	250	50	52	6.7	25	24	5.3	51	30	6.6
75	500	36	32	6.8	27	26	5.7	83	60	6.6
	1,000	23	22	6.5	10	10	5.5	90	†	6.7
	2,000	11	12	6.6	0	0	5.5	95	80	6.8
	3,000	2	3	6.4	0	0	5.7	†	†	6.6
	0	60	50	6.6	0	0	5.8	†	†	7.2
	50	100	85	6.7	60	70	5.9	†	†	7.2
	250	60	55	6.8	30	30	5.8	†	†	6.8
100	500	42	33	6.8	30	32	5.7	†	†	6.8
	1,000	30	32	6.6	21	20	5.6	†	†	6.8
	2,000	13	15	6.7	0	0	5.6	†	†	6.8
	3,000	0	0	6.6	0	0	5.8	†	†	6.8

* Pots containing washed sand as a substratum received a general fertilizer application of:

pounds per acre

Magnesium sulfate... 15
Ferrous sulfate.. 10
Potassium hydroxide.. 61
Calcium carbonate... 500

† Indicates that no plant growth was obtained.

loam, and Penn loam which were respectively 99.36, 70.23 and 47.10 per cent sand. The plant food in the substrata varied almost directly with their fineness. Largely as a result of their mechanical composition the soils differed in their water-holding capacities, which were 25, 35, and 68 per cent respectively. The acid phosphate was applied to the several substrata at the rates indicated in table 2. These applications caused the soils to have contents of available phosphate varying from the absolute minimum to an excess far beyond that which is reached in good farming practice. In the case where no phosphate was added to the washed sand it is estimated that there was present less than two pounds of available phosphate per acre which represents that in the seeds. In the case of the washed sand a general fertilizer application was made to all the pots as indicated in table 2. The data collected indicate that equal applications of phosphate do not have the same effect upon nodulation when the plants are grown in different substrata. This was naturally to be expected as the various substrata differed greatly in their properties. In the case of the washed sand where unknown factors were at a minimum the maximum nodulation was obtained when no phosphate was applied. This is taken as an indication that phosphate is not essential for nodulation. With the sand as a substratum the decreasing nodulation with increasing applications of phosphate is attributed to an increased osmotic pressure, or some similar factor. No attempt was made to explain the erratic results obtained when sassafras loam was the substratum. They are presented to emphasize the point that in soils many unknown factors play a part in the process of nodulation. In the pots where no plant growth was obtained germination was prevented by the high water content. The results obtained with Penn loam agree very well with the results obtained with the washed sand even though the Penn loam contained a large amount of phosphorus at the start.

The conclusion drawn is that phosphate is not essential for the nodulation of young soy bean plants. In connection with this conclusion it should be born in mind that soy beans are good foragers for phosphate. A close relation between root development and nodulation was noted as they increased and decreased together.

EXPERIMENT 3. EFFECT OF POTASH UPON NODULATION

This experiment was similar to experiment 2. Potassium, as the varying element, was applied as potassium chloride at rates of 0, 50, 250, 500, 1000, and 3000 pounds per acre. The substratum used was washed sand maintained at four different degrees of saturation. The washed sand only was used as a substratum as the data obtained from the true soils was considered to be of scant value. From the number of nodules appearing upon the roots of the several plants it may be assumed that the presence of potassium is unnecessary for maximum infection to occur. It would appear that in the series maintained at maximum saturation small applications of potash aided nodulation; but as

the increase is not greater than the experimental error it is of doubtful significance. Applications of potassium chloride up to and including 500 pounds per acre had no appreciable effect upon nodulation and greater applications inhibited the symbiotic relationship. This toxicity is probably due to an excess

TABLE 3

Effect of increasing applications of potassium chloride upon nodulation

POT NUMBER	SATURATION OF SUB-STRATUM	POTASSIUM CHLORIDE APPLIED PER ACRE*	REACTION OF SUBSTRATUM AFTER 2 WEEKS' GROWTH	NUMBER OF NODULES PER 10 PLANTS		AVERAGE WEIGHT AIR-DRY TOPS
				First	Second	
	per cent	*pounds*	*pH*			*gm.*
1 A	25	0	6.6	60	65	0.96
2 A	25	50	6.4	56	53	0.97
3 A	25	250	6.6	53	67	1.19
4 A	25	500	6.7	40	48	1.23
5 A	25	1,000	6.5	32	38	1.05
6 A	25	3,000	6.7	0	0	†
1 B	50	0	6.5	75	91	1.03
2 B	50	50	6.6	86	80	1.19
3 B	50	250	6.6	73	93	1.36
4 B	50	500	6.6	85	73	1.46
5 B	50	1,000	6.7	65	70	1.39
6 B	50	3,000	6.7	0	0	†
1 C	75	0	6.7	72	84	1.07
2 C	75	50	6.7	83	80	1.27
3 C	75	250	6.5	69	92	1.69
4 C	75	500	6.5	80	87	1.88
5 C	75	1,000	6.8	71	79	1.72
6 C	75	3,000	6.8	0	0	†
1 D	100	0	6.5	97	95	1.35
2 D	100	50	6.5	90	103	1.45
3 D	100	250	6.6	98	92	1.62
4 D	100	500	6.7	93	107	2.01
5 D	100	1,000	6.7	101	118	1.88
6 D	100	3,000	6.6	30	42	1.25

* All pots received a general fertilizer application of:

pounds per acre

Magnesium sulfate.. 15
Ferrous sulfate.. 10
Calcium carbonate.. 500
Phosphoric acid... 108

† Scant growth obtained.

of the potassium or chlorine ion, the high osmotic pressure or some similar factor.

The conclusion reached is that applications of potash are not necessary for maximum nodulation.

EXPERIMENT 4. EFFECT OF LIME UPON NODULATION

This experiment was similar to experiments 2 and 3 with calcium as the varying element.   The calcium was applied to washed sand at rates of 0, 50, 250, 500, 1000, 3000, and 5000 pounds per acre.   The sand was fertilized as

TABLE 4

Effect of increasing applications of calcium carbonate upon nodulation

POT NUMBER	SATURATION OF SUBSTRATUM	CALCIUM CARBONATE APPLIED PER ACRE*	REACTION OF SUBSTRATUM AFTER 2 WEEKS' GROWTH	NUMBER OF NODULES PER 10 PLANTS		AVERAGE WEIGHT AIR-DRY TOPS
				First	Second	
	per cent	*pounds*	*pH*			*gm.*
1 A	25	0	6.9	7	8	0.95
2 A	25	50	6.5	18	12	0.99
3 A	25	250	6.8	31	43	1.04
4 A	25	500	6.9	60	76	0.97
5 A	25	1,000	7.2	61	67	0.92
6 A	25	3,000	7.0	70	70	0.97
7 A	25	5,000	7.3	47	40	0.92
1 B	50	0	6.7	4	20	1.12
2 B	50	50	6.9	14	19	1.11
3 B	50	250	6.9	40	27	1.15
4 B	50	500	7.1	60	55	0.95
5 B	50	1,000	6.7	60	60	1.01
6 B	50	3,000	7.0	98	85	0.97
7 B	50	5,000	7.0	94	83	1.11
1 C	75	0	6.5	7	6	1.23
2 C	75	50	6.6	12	16	1.12
3 C	75	250	6.5	55	57	1.18
4 C	75	500	7.1	122	†	1.13
5 C	75	1,000	7.0	88	89	1.01
6 C	75	3,000	7.2	115	92	0.97
7 C	75	5,000	7.0	106	91	1.09
1 D	100	0	6.5	9	11	1.34
2 D	100	50	6.6	8	20	1.29
3 D	100	250	6.4	60	59	1.34
4 D	100	500	7.0	151	103	1.43
5 D	100	1,000	7.0	132	124	1.25
6 D	100	3,000	7.3	108	136	1.22
7 D	100	5,000	7.0	142	126	1.25

* All pots received a general fertilizer application of:

pounds per acre

Magnesium sulfate.. 15
Ferrous sulfate... 10
Potassium hydroxide.. 61
Phosphoric acid.. 108

† Pot broken, no results obtained.

indicated in table 4 and was maintained at four different degrees of saturation. The results obtained agree fairly well with those obtained in experiment 1, as maximum nodulation was not obtained with applications of limestone under 500 pounds per acre and larger applications did not cause increased nodulation. Since nodulation was extremely limited in the absence of calcium, it may be concluded that calcium is essential for good nodulation. It was noted that the root development of plants having scant nodulation was poor, while top growth was fair. The nature of the relation between poor root development, poor nodulation, and fair top growth is not clear and therefore will not be discussed at this time.

TABLE 5

Effect of increasing applications of sodium nitrate upon nodulation

POT NUMBER	SATURATION OF SUBSTRATUM	SODIUM NITRATE APPLIED PER ACRE*	REACTION OF SUBSTRATUM AFTER 2 WEEKS' GROWTH	NUMBER OF NODULES PER 10 PLANTS	
				First	Second
	per cent	*pounds*	*pH*		
1	75	0	6.8	49	41
2	75	50	6.9	72	48
3	75	250	6 8	45	61
4	75	500	7.1	8	12
5	75	1,000	7.2	0	0
6	75	3,000	7.0	0	0

* All pots received a general fertilizer application of:

	pounds per acre
Magnesium sulfate	15
Ferrous sulfate	10
Potassium hydroxide	61
Phosphoric acid	108
Calcium carbonate	500

EXPERIMENT 5. EFFECT OF NITROGEN UPON NODULATION

While a study of the effect of nitrogen upon nodulation is somewhat different from the other studies reported in this paper, as atmospheric nitrogen is always potentially available to inoculated legumes, the study has been made to round out the work. The general outline of the nitrogen work is similar to the outlines used in the work upon the other elements. The substratum used was washed sand which was fertilized as indicated in table 5. Only one degree of saturation was used however. The results obtained indicate that small applications of nitrogen increase nodulation to a slight degree, but that fixed nitrogen is not essential for good nodulation and that high applications inhibit the infection of the host.

CONCLUSIONS

1. Elements essential for plant growth do not directly affect the infection and nodulation of legumes.

2. A high degree of saturation favors nodulation.

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A NOTE ON THE NODULATION OF SOY BEANS[1]

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In the preceding paper (1) the conclusion was drawn that elements essential for plant growth do not directly affect the infection and subsequent nodulation of leguminous plants. In reaching this conclusion consideration was given to the fact that maximum nodulation was obtained in the absence of phosphorus and potassium. In the present paper a report is made of work carried out to determine possible reasons why essential elements favor nodulation under agricultural conditions and often tend to limit it under the conditions of these experiments. Consideration has been given to calcium as well as potassium and phosphorus.

METHODS

The methods followed were those outlined in the preceding paper and will be described here briefly only. A uniform plant stand was obtained in a series of pots filled with washed, fertilized quartz sand.—The crop grown was *Virginia* soy beans. Harvests and nodular counts were made four weeks after the seeds had germinated. Each pot held three pounds of sand which was maintained 75 per cent saturated, unless otherwise stated, by daily waterings with distilled water.

EXPERIMENT 1. EFFECT OF PHOSPHATE AND OSMOTIC PRESSURE UPON NODULATION

In an attempt to determine why acid phosphate inhibits nodulation, comparisons were made of the effect upon nodulation of increasing applications of acid and rock phosphate. Studies were also made of the effect upon nodulation of increasing osmotic pressures as governed by increasing fertilizer applications and amount of water in the substratum. The possible effect of acidity induced by acid phosphate has been considered.

TABLE 1

Effect of increasing applications of acid and rock phosphate upon the nodulation of Virginia soy beans

SATURA-TION OF SUB-TRACTUM	PHOS-PHATE FERTILIZER APPLIED PER ACRE	ACID PHOSPHATE SERIES				ROCK PHOSPHATE SERIES			
		Reaction after 2 weeks growth	Nodules per 10 plants, average of 2 pots	Weight of air dried crop	Lowering of freezing point	Reaction after 2 weeks growth	Nodules per 10 plants, average of 2 pots	Weight of air dried crop	Lowering of freezing point
per cent	*lbs.*	*pH*		*gm.*	*°C.*	*pH*		*gm.*	*°C.*
25	0	6.4	50	1.59	0.03	6.5	53	1.56	0.03
25	50	6.4	78	1.33	0.03	6.6	65	1.55	0.03
25	250	6.4	63	1.55	0.04	6.5	76	1.60	0.03
25	500	6.3	24	1.45	0.05	6.5	78	1.60	0.03
25	1000	6.4	27	1.49	0.06	6.4	64	1.58	0.03
25	2000	6.4	40	1.24	0.16	6.4	64	1.62	0.03
25	3000	6.4	7	0.86	0.20	6.3	63	1.63	0.03
25	5000	6.3	0	0.57	0.20	6.2	64	1.65	0.04
50	0	6.4	120	1.74	0.01	6.4	108	1.71	0 02
50	50	6 5	115	1 67	0.01	6.5	109	1.68	0.02
50	250	6 4	110	1.45	0.02	6.5	99	1.82	0.02
50	500	6.4	96	1.54	0.02	6.5	108	1.62	0 02
50	1000	6.3	69	1.53	0.03	6.4	93	1.68	0.02
50	2000	6.4	48	1.36	0.07	6.3	102	1.73	0.02
50	3000	6.3	14	0.94	0.08	6.1	100	1.62	0 02
50	5000	6.4	0	0.70	0.12	6.3	105	1.72	0.02
75	0	6.4	123	2.09	0.01	6.4	122	2.25	0.01
75	50	6.5	118	2.07	0.00	6.5	97	2.08	0.01
75	250	6.4	120	1.81	0.01	6.5	99	2.28	0.01
75	500	6.4	100	2.03	0.02	6.5	90	2.28	0.01
75	1000	6.3	75	2.16	0.02	6.4	101	2.30	0.01
75	2000	6.4	40	1.51	0.05	6.3	94	2.17	0.01
75	3000	6.3	24	1.12	0.06	6.3	97	2.19	0.01
75	5000	6.3	3	1.02	0.09	6.2	103	2.22	0.01
100	0	6.2	87	1 78	0.01	6.3	93	2.18	0.01
100	50	6.5	75	1.99	0.00	6.5	82	1.83	0.01
100	250	6.3	94	1.88	0.01	6.4	99	1.96	0.01
100	500	6.4	85	1.97	0.01	6.5	99	1.82	0.01
100	1000	6.3	84	2.18	0.02	6.4	86	1.96	0.01
100	2000	6.4	41	1.97	0.03	6.2	92	2.00	0.01
100	3000	6.3	0	1.02	0.07	6.1	82	1.97	0.01
100	5000	6.3	0	0.82	0.08	6.2	87	1.88	0.01

All pots received a general fertilizer application of:

lbs. per acre

Magnesium sulfate... 15
Ferrous sulfate... 10
Calcium carbonate.. 500
Potassium hydroxide... 61

The data in table 1 show that under the conditions of the experiment rock phosphate had no appreciable effect upon the nodulation of soy beans. Practically the same degree of nodulation was obtained when an application of rock phosphate was made at the rate of five thousand pounds per acre, as when no phosphate was present in the substratum; while an application of one thousand pounds of acid phosphate materially reduced nodulation. In view of these facts it is evident that the toxicity of acid phosphate to nodulation is in some way associated with its solubility.

This toxicity might be due to an increased acidity, an increased osmotic pressure, or some physiological effect upon the host, infecting bacteria, or the symbiotic relationship.

TABLE 2

Effect of osmotic pressure upon nodulation

POT NUMBER	FERTILIZER APPLICATION*	SATURATION OF SUBSTRATUM	LOWERING OF FREEZING POINT	NODULES PER 10 PLANTS	
				Pot a	Pot b
		per cent	°C.	.	
1	Normal	25	0.05	10	15
2	Normal	50	0.02	21	33
3	Normal	75	0.02	28	36
4	Normal	100	0.01	39	32
5	Normal	25	0.05	11	13
6	Twice normal	50	0 05	27	31
7	Three times normal	75	0.05	34	30
8	Four times normal	100	0.05	49	35

*A normal fertilizer application was:

	lbs. per acre
Magnesium sulfate	15
Ferrous sulfate	10
Calcium carbonate	500
Potassium hydroxide	61
Acid phosphate	500

That the acidity is not the factor which limits nodulation is evidenced by the fact that active acidity as indicated by pH values remained practically unchanged even after the largest addition of acid phosphate.

That the osmotic pressure is not the limiting factor is shown by the data in tables 1 and 2. In table 1 it is seen that although nodulation varies indirectly with osmotic pressure, whether the osmotic pressure be varied by altering fertilizer application or water content of the substratum, this variation is not constant. When the substratum is 25 per cent saturated and fertilizer applications have reduced the freezing point 0.20°C., nodulation is inhibited; but when the substratum is 100 per cent saturated nodulation is limited by a lowering of the freezing point by only 0.07 degrees. With the above data in mind the work as outlined in table 2 was carried out. Here in one case the

salt application was maintained constant while the degree of saturation was increased with a resulting decrease in osmotic pressure, and in the other case osmotic pressure was maintained constant by increasing fertilizer applications as the degree of saturation was increased.   The results obtained clearly indicate that there is little relation between osmotic pressure (in the degrees obtained in this experiment) and nodulation.   If there is any relation it is such that the relation between moisture content of the substratum and nodulation completely hides it.

Considering table 2, the fact that the relation between fertilizer application and osmotic pressure was so easily obtained is attributed to the fact that the substratum was washed sand which has a very small power of adsorption.

In view of these facts and the fact that nodulation tends to decrease as plant growth decreases, it may be assumed that acid phosphate limits nodulation by affecting some physiological activity of the plant.

Studies of the effect of acid phosphate upon the toxicity of certain minerals to nodulation will be reported under experiment 3.

EXPERIMENT 2.   THE EFFECT OF LIME UPON NODULATION

In the preceding paper (1) the only element reported as increasing nodulation was calcium.   Theoretical considerations show that calcium might aid nodulation by:

1. Eliminating the effect of acid radicals
2. Counteracting the effect of non-acid toxic ions
3. Entering into the mechanism of infection or nitrogen fixation
4. Being the element which would first limit the growth of soy bean seedlings

That under the conditions of these experiments calcium does not aid nodulation by neutralizing the effects of acid radicals is shown by the data in table 3. Here the acidity was completely neutralized by the addition of a non calcic base and in spite of this neutralization increasing applications of lime increased nodulation in approximately the same degree as when the non calcic base had not been added.   It has also been noted that good nodulation may take place at pH values lower than those at which nodulation was limited by the lack of lime.

That calcium can neutralize the toxic effect of certain mineral substances is shown by the results give in table 4.   The toxic substance to be counteracted in this case was acid phosphate a substance which readily reacts with lime. The acid phosphate was applied at the rate of five thousand pounds per acre, an amount which will completely inhibit nodulation.   The control series which received an application of acid phosphate at the rate of 135 pounds per acre shows the effect of increasing applications of lime in the absence of a toxic phosphate application.   The results obtained indicate that when the pots are seeded immediately after being prepared, increasing applications of lime

have little beneficial effect upon nodulation; but that when time is allowed for the phosphate and lime to react applications of lime increase nodulation.

Some consideration as to the effect of lime upon the toxicity to nodulation induced by applications of other minerals is given under experiment 3.

TABLE 3

Effect of increasing applications of lime upon nodulation in a substratum neutralized by a noncalcic base

POT NUMBER	CALCIUM CARBONATE APPLIED PER ACRE	NEUTRALIZATION OF SOIL	REACTION AFTER 2 WEEKS GROWTH	NUMBER NODULES PER 10 PLANTS, AVERAGE 2 POTS
	lbs.		*pH*	
1	0	0.07 gm. NaOH per pot	7.1	2
2	50		7.2	16
3	250		7.1	20
4	500		7.3	37
5	1000		7.2	43
6	3000		7.2	49
				.
A1	0	0.25 gm. Na$_2$CO$_3$ per pot	7.0	8
A2	50		6.9	11
A3	250		7.1	27
A4	500		7.2	42
A5	1000		7.2	48
A6	3000		7.3	51
B1	0	Not neutralized	5.6	15
B2	50		5.8	18
B3	250		6.0	46
B4	500		6.4	55
B5	1000		6.6	67
B6	3000		6.7	54

The substratum in all pots was maintained 75 per cent saturated.
Substratum was washed quartz sand fertilized with:

	lbs. per acre
Magnesium sulfate...	15
Ferrous sulfate.	10
Potassium hydroxide	61
Acid phosphate.	135

That calcium either enters into the mechanism of infection and nitrogen fixation or is the element which limits the growth of the seedlings seems probable since the poorest developed plants in the lime series were those that had received little or no lime. The plants in pot 27 (table 4) were of much better color etc., than the plants in pot 21 even though air-dry weights indicate that both sets of plants were equally developed.

TABLE 4

Effect of increasing applications of calcium carbonate upon nodulation in the presence of an excess of acid phosphate

POT NUMBER	CALCIUM CARBONATE APPLIED PER ACRE	REACTION AFTER 2 WEEKS GROWTH	NUMBER NODULES PER 10 PLANTS, AVERAGE 2 POTS	WEIGHT OF AIR DRIED CROP
	lbs.	*pH*		*gm.*
1	0	5.6	15	....
2	50	5.8	18	....
3	250	6.0	46	....
4	500	6.4	55	...
5	1000	6 6	67	. ..
6	3000	6.7	54	. ..
11	0	5.5	0	0.00
12	50	5.8	0	0.00
13	250	5 7	0	0.00
14	500	5.9	0	scant
15	1000	5.9	0	scant
16	3000	6.4	0	scant
17	5000	6.4	8	scant
21	0	5 6	2	1.06
23	250	5.7	20	0.95
24	500	5.8	25	0.91
25	1000	5.9	31	1.02
26	3000	6.0	52	0.98
27	5000	6.5	77	1 06

Pots numbered 1 to 6 received 135 pounds of acid phosphate per acre.

Pots numbered 11 to 17 received 5000 pounds of acid phosphate per acre and were planted immediately after application of fertilizers.

Pots numbered 21 to 27 received 5000 pounds of acid phosphate per acre and were planted three weeks after application of fertilizers.

All pots received a general fertilizer application of:

	lbs. per acre
Magnesium sulfate...	15
Ferrous sulfate..	10
Potassium hydroxide...	61

EXPERIMENT 3. EFFECT OF INCREASING APPLICATIONS OF ESSENTIAL ELEMENTS UPON TOXICITY TO NODULATION INDUCED BY NON-ESSENTIAL ELEMENTS

From the data presented in this and the preceding paper no explanation can be made for the fact that various investigators have found that applications of essential elements benefit nodulation. Since the manner in which the elements studied affect the nodulation of young plants is at best uncertain it is possible that when they do favor nodulation they do so by counteracting something that is toxic to nodulation. In view of this consideration the applications of iron, aluminum, copper and manganese toxic to nodulation were determined.

TABLE 5

Effect of increasing applications of mineral fertilizers upon toxicity to nodulation induced by certain minerals

TOXIC MINERAL APPLIED	FERTILIZER APPLICATION PER ACRE	NUMBER NODULES PER 10 PLANTS—AVERAGE FOR 2 POTS		
		Acid phosphate series	Potassium chloride series	Calcium carbonate series
	lbs.			
None	0	92	40	10
	50	86	33	17
	250	79	39	30
	500	70	28	35
	1000	29	24	38
	3000	11	6	40
FeSO$_4$	0	3	25	0
	50	17	129	8
	250	27	21	10
	500	20	12	11
	1000	4	4	12
	3000	1	0	70
AlSO$_4$	0	10	21	0
	50	5	20	3
	250	22	17	3
	500	6	22	7
	1000	0	7	6
	3000	0	0	19
CuSO$_4$	0	0		
	50	0		
	250	0		
	500	0		
	1000	0		
	3000	0		
MnSO$_4$	0	9		
	50	21		
	250	42		
	500	33		
	1000	21		
	3000	0		

All pots received a general fertilizer application of 15 pounds of magnesium sulfate per acre and 10 pounds ferrous sulfate per acre.

The acid phosphate series also received 61 pounds of potassium hydroxide and 500 pounds of calcium carbonate per acre.

The calcium carbonate series also received 61 pounds of potassium hydroxide and 135 pounds of acid phosphate per acre.

The potassium chloride pots also received 500 pounds of calcium carbonate and 135 pounds of acid phosphate per acre.

The substratum was washed sand maintained 75 per cent saturated.

Iron was chosen because it is a mineral found in most soils and affects plants under acid conditions. Aluminum was chosen for the same reasons. Copper was selected because it is an element toxic to plant activities even though rarely present in the soil in large amounts. Manganese was selected because past studies have shown that small applications of it affect nodulation to a large extent. All of these elements were applied as the sulfate in amounts which hot house tests demonstrated to be toxic to nodulation. The amounts used were:

$$0.3418 \text{ gms. Fe SO}_4 \cdot 7\text{H}_2\text{O per pot}$$
$$0.6836 \text{ gms. AlSO}_4 \cdot 18\text{H}_2\text{O per pot}$$
$$0.1709 \text{ gms. CuSO}_4 \cdot 5\text{H}_2\text{O per pot}$$
$$0.1709 \text{ gms. MnSO}_4 \cdot 4\text{H}_2\text{O per pot}$$

The results obtained from increasing applications of mineral fertilizers are given in table 5.

These results indicate that acid phosphate reduces the toxicity to nodulation caused by an excess of iron, aluminum, or manganese; that potassium chloride may reduce the toxicity to nodulation resulting from an excess of iron or alumium; and that calcium carbonate may reduce the toxicity of an excess of acid phosphate (see table 4). Applications of calcium probably reduce the toxicity of iron and aluminum; but this is not definite since when no calcium was present nodulation was limited by the lack of lime as well as the toxicity of the mineral elements.

GENERAL DISCUSSION AND CONCLUSIONS

From the literature it is evident that under general farming conditions applications of phosphorus and potassium and calcium increase nodulation. The manner in which these elements affect nodulation is at best problematical. From the data presented it is seen that all three elements under consideration may increase nodulation by counteracting factors limiting this process. Calcium in addition to this power seems either to enter into the mechanism of infection and subsequent fixation of nitrogen or to be the element which would first become the limiting factor in the growth of the seedlings. In consideration of the above discussion and data presented the following conclusions have been drawn.

1. When phosphorus and potassium increase nodulation they may do so by counteracting some toxic factor in the soil.

2. When calcium increases nodulation it may do so by counteracting some toxic factor in the soil, by entering directly into either the process of infection or nitrogen fixation, or as a result of being the first element to limit the growth of the seedlings by its absence.

3. Under the conditions of these experiments when the elements under consideration affect nodulation they may possibly do so by disturbing the physiological activities of the plants.

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THE VALUE OF SOIL ANALYSIS WHEN LIMITED TO AN INTENSIVE SINGLE CROPPING SYSTEM

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In studying the interrelations of soils and plants, soil analysis as an indication of fertilizer requirements or as a measure of plant food availability appears to conflict with certain modern views. Experimental tendencies are now directed toward a more complete knowledge of the inherent physiological properties of plants as influenced by variations in the plant food balance. This is due to the failure to definitely associate the analysis of the soil with variations in plant growth and adaptation. There are undoubtedly thoroughy sound principles on which to base such tendencies. A knowledge of the total mineral nutrient content of the soil or that which is soluble in strong acids is practically valueless for immediate crops without some knowledge of the availability. It has some value as a measure of reserve plant food, marked deficiencies or abundance being usually indicated, but this is of minor importance as compared to the forms in which these nutrients are present. The possible combinations in the soil are legion and in order to detect changes in soil composition which result from fertilizer applications, which amounts are sufficient to stimulate plant growth, it is necessary to resort to the use of water or dilute acids. Determination of the effect of a fertilizer application is not within the range of the accuracy of concentrated solvents.

In Hawaiian soils, the high colloidal content of which imparts strong fixing properties, little success has thus far attended the use of water extracts. This is especially true with phosphates. Dilute acids, therefore, appear to be the only possible recourse on such soil types in which low reserve plant food content is rarely noted. Even here fixation in the presence of the solvent is a notable factor.

Sugar cane appears to make heavy demands upon the mineral nutrients at certain definite stages of growth. It is evident that a measure of available plant food is of greater value than a water extract which is too greatly influenced by the high fixing power of our soils. With our crop, adequate supplies of available plant food and the rate at which the replenishment of the soil solution is possible, are the important factors rather than the actual concentration of the soil solution at any period. The solvent, in order to be of value in soil analysis, should show some definite relation between the

soil and the food requirement of the crop. The value of any method, therefore, depends on the accuracy with which this analysis can be accomplished. On this basis we have a point in favor of dilute acids.

Lack of thoroughly sound theoretical principles on which to base the extraction of the soil with dilute acids must be admitted. It is true that the solvent properties of dilute acids for definite phosphate or potash compounds can be accurately determined, but when applied to soil conditions other factors will more or less influence solubility, thus limiting the general application of this property. The only possible value of dilute acids lies in the empirical establishment of a working agreement between the extraction of mineral nutrients and response of a soil type to fertilization. In other words it is essential to corroborate the chemical analysis with numerous field experiments and a knowledge of the feeding power and other peculiarities of the crop,

In the Hawaiian Islands, approximately 225,000 acres are devoted to the culture of sugar cane. The conditions so far as this crop is concerned are as follows. We are dealing with one crop and are therefore concerned only with such variation in feeding power as might exist between different varieties. While we have quite a wide variation in soil types the lands cultivated to sugar cane involve only the lowland sections usually skirting the shore line of the islands. Cropping is continuous and fallowing or rotation rarely practiced, so the soil is never at rest. In such a continuous system of cropping there is a constant drain on the plant nutrients and less opportunity for the natural agents such as aeration and fallowing to increase the availability of plant food in the soil.

A survey of crop reports shows a wide variation in yields per acre in the different sections of the Islands or even on the same plantation. This variation is due mainly to environment, temperature, exposure and moisture supply. Variation in mineral nutrients present in the soil is only a minor factor in comparison. On the other hand the extensive field experiments, conducted by this experiment station, have noted definite areas in which phosphate and potash deficiencies are a limiting factor. Composite soil samples have been taken from a number of these experiments submitted to various methods of analysis and the results compared with the known history of the soil. The comparative value of these methods is strikingly illustrated by the data thus obtained.

<div align="center">PHOSPHATES</div>

Details covering methods of analysis are obviously outside the scope of this article. Suffice it to say that total P_2O_5 was determined by fusion with sodium carbonate; extraction with concentrated HNO_4 by digesting 2 gm. soil with 30 cc. acid for twenty hours on the steam bath; extraction with concentrated HCl by the so called agricultural method; extraction with 1 per cent citric acid by shaking 100 gm. soil with 1 liter solvent for six hours;

extraction with 0.2 N nitric acid by digesting 120 gm. of soil with 1200 cc. acid for five hours at 40°C. The results are given in table 1.

TABLE 1

Analyses of soils from phosphate experiments

SOIL NUMBER	TOTAL	BY CONCENTRATED HNO₂	BY CONCENTRATED HCl	BY 1 PER CENT CITRIC	BY 0.2 N I:NO₂
Per cent of P_2O_5 in soils giving no response					
3578	0.46	0.34	0.30	0.0030	0.00051
405	0.42	0.36	0.33	0.0035	0.00121
844	0.55	0.34	0.22	0.0228	0.00410
872	0.60	0.26	0.20	0.0726	0.02480
239	1.06	1.04	0.94	0.0441	0.07920
3	1.13	0.70	0.50	0.3190	0.16280
538	0.47	0.35	0.38	0.0034	0.00048
318	0.42	0.35	0.25	0.1283	0.00950
418	0.23	0.16	0.12	0.0030	0.00040
7103	0.57	0.30	0.24	0.0164	0.00510
5493	0.95	0.66	0.18	0.0049	0.00093
7658	1.06	0.66	0.41	0.0058	0.00080
10781	1.66	1.17	0.46	0.0176	0.00420
Per cent of P_2O_5 in soils giving response					
3460	0.38	0.25	0.21	0.0014	0.00028
3985	0.46	0.21	0.24	0.0009	0.00026
996	0.24	0.16	0.11	0.0008	0.00015
998	0.57	0.46	0.45	0.0028	0.00034
999	0.56	0.43	0.38	0.0024	0.00037
444	0.28	0.13	0.16	0.0024	0.00060
750	0.25	0.16	0.15	0.0027	0.00060
621	0.21	0.13	0.06	0.0011	0.00038
7147	0.17	0.12	0.04	0.0009	0.00023

TABLE 2

Showing maximum, minimum and average P_2O_5 as measured by 1 per cent citric and 0.2 N nitric acids

	1 PER CENT CITRIC	0.2 N NITRIC
Per cent of P_2O_5 in soils giving no response		
Average...	0.0493	0.02260
Maximum..	0.3190	0.16280
Munimum..	0.0030	0.00040
Per cent of P_2O_5 in soils giving response		
Average...	0.0017	0.00034
Maximum..	0.0028	0.00060
Minimum..	0.0008	0.00015

The results obtained by fusion and solubility in strong nitric and hydrochloric acids warrant little comment.   Few Hawaiian soils are lacking in reserve phosphate.   On the other hand it will be noted that there is a marked correlation between the phosphate content as measured by 0.2 N nitric acid and 1 per cent citric and response of sugar cane to phosphate manuring on our island soils.   These figures are further presented in condensed form in table 2.

In view of the above, certain solvent properties of these acids were studied in order to arrive at a better comparison of their values.   In brief these results showed a surprising absorption of P_2O_5 by the soil in contact with 0.2 N nitric acid which was true to a far less extent of 1 per cent citric acid.   This lesser degree of fixation in the presence of solvent, a greater solvent power, absence of the effect of amount of acid neutralized during extraction and the fact that the P_2O_5 soluble in 1 per cent citric acid is completely removed in one extraction indicated this solvent to be better adapted to our requirements.   In this series of soil samples taken from twenty-three field experiments located on fifteen different plantations including four islands, all soils containing less than 0.003 per cent $P_2 O_5$ soluble in 1 per cent citric acid responded to phosphates.   This solvent therefore merits consideration as a measure of available phosphoric acid in Hawaiian soils cropped to sugar cane.

POTASH

Applying these same methods of analysis, with the exception of concentrated nitric acid which was omitted, and total K_2O in which the soil was decomposed by hydroflouric, nitric and sulfuric acids, to composite samples of soil taken from potash field experiments the results which were obtained are given in table 3.

Here, again, we note a high reserve potash content usually present and little or no relation between total potash soluble in concentrated HCl and potash fertility.   On the other hand there will be noted a decided relation between K_2O as determined by 1 per cent citric acid and response of the soil to potash fertilization.   For the soils in which field experiments showed a deficiency of available potash, the determinations varied from 0.009 to 0.023 per cent, with an average of 0.014 per cent.   Those soils which appear to be amply supplied with available potash, were shown to contain 0.031 to 0.082 per cent K_2O soluble in 1 per cent citric acid with an average of 0.054 per cent.   In other words, no soil containing more than 0.023 per cent K_2O gave profitable returns from potash manuring.   Analysis of extracts made with 0.2 N nitric acid gave results of little or no value.

These soil samples were taken from fourteen field experiments located on thirteen different plantations on four islands and indicate the value which may be attached to the results obtained by this method.

TABLE 3

Analyses of soils from potash experiments

SOIL NUMBER	TOTAL	BY CONCENTRATED HCl	BY 1 PER CENT CITRIC	BY 0.2 N HNO₃
Per cent K_2O in soils giving no response				
239	2.95	2.14	0.054	0.051
3	1.61	0.43	0.065	0.122
7502	1.04	0.52	0.050	0.070
7225	0.38	0.32	0.055	0.038
405	1.05	0.49	0.049	0.050
710	1.10	0.52	0.082	0.223
999	1.12	0.38	0.031	0.063
Per cent K_2O in soils giving response				
7658	0.66	0.31	0.017	0.042
10970	0.54	0.33	0.012	0.014
11014	0.65	0.21	0.011	0.012
7692	0.95	0.35	0.023	0.045
10703	0.79	0.38	0.009	0.025
3985	0.67	0.40	0.015	0.034
11462	0.46	0.15	0.014	0.092

DISCUSSION

It is not suggested that there is any evidence of the existance of two definite groups of phosphate or potash compounds, available and unavailable but, rather that they may be present in the soil in different degrees of disintegration and therefore, availability. In such a complex material as soil, it is not possible to select a solvent which will dissolve any definite phosphate or potash compound exclusive of another in entirety. Results obtained on our island soils do, however, show a higher calcium phosphate content in the coral impregnated areas with iron and aluminum phosphates predominating in other types, even though the coral soils are very high in iron and aluminum.

Again the general adaptation of this method is not advocated. Local conditions are admittedly specific. The influence of variation in soil types and feeding power of plants is known to be a factor. This point is clearly indicated by a comparison with the work of Dyer (2) who considered a soil deficient in plant food if it contained 0.01 per cent P_2O_5 or 0.005 per cent K_2O; Hall and Plymen (5) who suggested 0.02 per cent for P_2O_5; Wood and Berry (10) who suggested 0.02 per cent for P_2O_5 and 0.01 per cent for K_2O; Tempany (9) who considered 0.005 per cent low and 0.01 per cent high for P_2O_5, and Dunlop (1) who advised manuring for soils containing less than 0.005 per cent P_2O_5 and 0.006 per cent K_2O.

Also, it may not be amiss to compare the figures obtained with 0.2 N nitric acid in which no soil containing more than 0.0006 per cent P_2O_5 responded to phosphate manuring with those of Snyder (7, 8) where all soils containing

0.0025 to 0.0083 per cent P_2O_5 gave response; the Texas Station (3) where a content of 0.002 per cent of P_2O_5 is considered deficient and the Wisconsin Station (6) where 0.015 per cent is considered low. In potash experiments, Snyder (7, 8) found 0.015 per cent K_2O in a soil giving response, Fraps (4) found all soils containing less than 0.005 per cent P_2O_5, 87 per cent deficient and those containing 0.005 to 0.015 per cent P_2O_5, 55 per cent deficient.

On the basis of the above investigation which will be published in detail in bulletin form, 1 per cent citric acid is being extensively applied to Hawaiian soils as a guide to fertilizer policy on the sugar plantations. It is further suggested that 1 per cent citric acid may be of considerable value under similar limited conditions. It should be mentioned however, that interpretation is not based entirely on chemical analysis alone. There has been noted a definite relation between forms of silica and lime present in Hawaiian soils as well as the soil reaction and availability of P_2O_5. Also that response to phosphate manuring is typical of upland areas and rarely obtained on lowland soils. The availability of potash appears to be influenced by the physical composition of the soil, lime content and reaction with an additional association of low availability in the districts of heavy rainfall. Consideration must therefore be given to the above factors and a more or less intimate knowledge of the properties and past performance of the soil type. The high feeding power of sugar cane for phosphoric acid is also considered. Recommendations from the above data are therefore suggested only as a matter of policy and not "laid down" as an infallible rule as variations are admitted.

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THE INFLUENCE OF SILICA, LIME AND SOIL REACTION UPON THE AVAILABILITY OF PHOSPHATES IN HIGHLY FERRUGINOUS SOILS

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The sugar lands of Hawaii are practically all located at the lower elevations skirting the shore line of the islands. In some cases the increase in altitude from the shore line is quite rapid but little cane culture is practiced above an elevation of 1500 feet. Extensive field experiments conducted by this experiment station have shown response to phosphate fertilization to be more or less typical of upland areas. On the other hand response is rarely noted on lowland soils. These observations suggested some inherent properties which would account for this apparent variation in phosphate availability. A chemical examination of thirty-nine soil samples collected from field experiments located on widely varying soil types on the four major islands, Hawaii, Maui, Kauai and Oahu indicated silica, lime and soil acidity to be the principal factors involved. Of the thirty-nine samples, fourteen gave response and twenty-five no response to phosphate fertilization.

RELATION OF SILICA TO AVAILABILITY

Pfeffer (6) classifies silica among the non-essential elements yet points out that in nature where competition is severe a non-essential element may be of decisive importance. In the ash of grasses, silica may form 50-80 per cent of the whole. This is a distinguishing feature of the Gramminae of which class sugar cane is a member. Maxwell (3) found 50-60 per cent silica in the ash of Hawaiian canes. At Rothamstead (1), sodium silicate has been applied in certain of their experiments over a long period and has caused a response similar to that noted on the phosphate plots. Schollenberger (7) has recently found a greater phosphate content in the crop grown with lime and silicate than where lime alone was used, the soil being the only source of phosphate.

In Hawaiian soils there is almost universally present large amounts of soluble silica although the total silica is considered very low. In the analyses of these thirty-nine samples, total SiO_2 varied from 14 to 35 per cent on the water free soil but there was no relation between this and the availability of P_2O_5. In a classification of the lime compounds of soils, Shorey, Fry and

Hazen (8) have assumed that 4 per cent HCl acts as a solvent for easily decomposible calcium silicates. On this basis 4 per cent HCl was used as the principal solvent in this soil series. Calcium silicate soluble in 1 per cent citric was also determined. The results are given in table 1.

There is shown in table 1 a marked relation between the solubility of silica in the soils from these field experiments and response to phosphate fertiliza-

TABLE 1

Relative solubility of silica in 1 per cent citric acid and 4 per cent hydrochloride acid

SOLUBILITY OF SiO₂ IN SOILS GIVING RESPONSE				SOLUBILITY OF SiO₂ IN SOILS GIVING NO RESPONSE			
Island	Soil number	Extracted with 1 per cent citric	Extracted with 4 per cent HCl	Island	Soil number	Extracted with 1 per cent citric	Extracted with 4 per cent HCl
		per cent	*per cent*				
	364	0.016	0.04	Kauai	375	0.14	0.25
	398	0.019	0.03		378	0.09	0.23
	995	0.008	0.04		405	0.10	0.25
Kauai	996	0.025	0.11				
	998	0.075	0.34	Oahu	844	0.16	0.71
	999	0.072	0.30		872	0.29	0.81
	1000	0.019	0.06		239	0.19	0.87
					3	1.24	1.25
	444	0.090	0.27		538	0.18	0.27
Oahu	750	0.088	0.33		318	0.22	0.34
					418	0.26	0.32
	621	0.125	0.21				
	714	0.089	0.25	Maui	710	0.13	0.30
	715	0.110	0.25		711	0.12	0.30
Maui	716	0.112	0.25		712	0.14	0.30
	717	0.105	0.25		713	0.12	0.30
				Hawaii	549	0.11	0.95
					551	0.11	1.28
					553	0.10	1.46
					765	0.11	0.83
					766	0.11	1.20
					767	0.10	0.99
					768	0.14	1.29
					1078	0.17	1.97
					1079	0.08	0.77
					1080	0.10	1.68
					1081	0.13	1.51

tion. This indicates that a greater availability of P₂O₅ will accompany a greater availability of silica. As for the relative assimilation of P₂O₅ from these soils by the cane the following observations are of interest. Soil 3 contains the highest citric soluble silica and is one of the highest in silica soluble in 4 per cent HCl. McAllep and Bomonti (4) have determined the phosphate content of juice from cane grown on this soil and found it to be

the highest in P_2O_5 yet examined, namely 0.10 per cent. The soils from the Hilo-Hamakua coast district of Hawaii have rarely shown response to phosphates. This section is represented in table 1 by the ten soils from Hawaii. These are high in the available forms of silica and the juices have been found to be uniformly high in P_2O_5. On the other hand juices from cane grown on soils 444 and 750 are very low in P_2O_5, that is 0.01 to 0.015 per cent. This was only very slightly increased by phosphate fertilization at the rate of 180 pounds P_2O_5 per acre although the yield of cane was greatly increased. In other words the results do not indicate that the percentage of P_2O_3 in the juice will be greatly increased by phosphate applications to a soil low in phosphates but rather that a supply of available silica is a factor in the assimilation.

<div align="center">LIME AND SOIL ACIDITY</div>

Frequent reference is to be noted in soil literature to the relation of lime and soil acidity to the availability of soil phosphates. It is now quite generally established that certain unproductive acid soils may be restored to normal by phosphate manuring as well as by liming. One example of such a soil has been noted here in Hawaii (2). Liming on an upland soil in the Haiku district on the Island of Maui failed to correct an apparent toxicity where phosphates produced large gains ranging from 80 to 500 per cent.

In determining the forms of lime present in these soils the procedure adopted by Shorey (8) involving the use of 2 per cent HCl as a solvent for calcium carbonate, calcium sulfate and so-called calcium-humus compounds and that of 4 per cent HCl for extracting additionally the easily decomposible silicates was used. The total lime was determined by fusion with Na_2CO_3. That soluble in water saturated with carbon dioxide was determined by shaking one part soil to five parts water for five hours in a shaking machine. Hydrogen-ion concentration was determined with the hydrogen electrode. The results are given in table 2 and calculated to the water-free basis.

The higher hydrogen-ion concentration in those soils giving response to phosphate fertilization is significant. The principal exceptions are the soils from the Island of Hawaii which are high in acidity yet do not respond to phosphates. These soils are a distinct type, highly hydrated and the acidity appears to be due to the presence of acid silicates developed from excessive rainfall and leaching of lime, magnesia, potash and soda which tend to maintain the alkalinity or neutrality of such compounds. The higher availability of phosphate in this soil type is probably associated with the high availability of silica and the high phosphate content. On the other soil types, no soil with a pH value above 6.3 showed any lack of available phosphate while with one exception all soils with a pH value of 6.3 or lower gave response.

A similar relation applies to lime and especially in regard to the relative solubility in water saturated with carbon dioxide. In general, those soils giving response to phosphates are lower in total lime present as carbonate

TABLE 2
Showing relation of hydrogen-ion concentration and lime to availability of P_2O_5

ISLAND	SOIL NUMBER	REACTION	TOTAL CaO	CaO SOLUTION 4 PER CENT HCl	CaO SOLUTION 2 PER CENT HCl	CaO SOLUBLE IN CARBONATED WATER
		pH	*per cent*	*per cent*	*per cent*	*p.p.m.*

Soils giving no response

ISLAND	SOIL NUMBER	REACTION	TOTAL CaO	CaO SOLUTION 4 PER CENT HCl	CaO SOLUTION 2 PER CENT HCl	CaO SOLUBLE IN CARBONATED WATER
Kauai	375	7.5	1.14	0.58	0.55	938
	378	6.6	1.29	0.79	0.27	503
	405	6.3	1.11	0.40	0 34	429
Oahu	844	6.6	1.43	0.87	0.74	448
	872	7.7	3.01	1 26	0.88	895
	239	8.1	6.90	6.18	4.21	2010
	3	8.2	2.66	1.55	1.16	1070
	538	7.7	1 23	0.26	0.24	352
	318	7.7	1 25	0.48	0.39	. . .
	418	7.3	1 02	0 34	0.30	. . . .
Maui	710	6.8	1 02	0 33	0.30	363
	711	6.8	1 02	0 33	0.30	363
	712	6.8	1.02	0.33	0.30	363
	713	6.8	1.02	0 33	0.30	363
Hawaii	549	6.4	1 31	0.64	0.62	588
	551	6 2	1 25	0 51	0.49	450
	553	6.1	1 11	0.47	0.46	445
	765	5.1	1 04	0.45	0 11	175
	766	5.3	0.96	0.46	0.10	175
	767	5.3	0.92	0 44	0.06	175
	768	5.6	1.11	0 52	0.14	207
	1078	5.0	0.94	0.17	0.16	137
	1079	5.1	0 88	0 16	0.15	137
	1080	5.1	0 88	0 17	0 12	137
	1081	5.1	0.99	0.18	0.15	137

Soils giving response

ISLAND	SOIL NUMBER	REACTION	TOTAL CaO	CaO SOLUTION 4 PER CENT HCl	CaO SOLUTION 2 PER CENT HCl	CaO SOLUBLE IN CARBONATED WATER
Kauai	364	4.6	0.81	0.10	0.07	99
	398	4.8	0.87	0.12	0.10	127
	995	5.3	0.56	0.33	0.24	179
	996*	6.8	1.52	1.18	1.05	1165
	998†	6.5	0.86	0.61	0.43	468
	999†	6.3	0.71	0.48	0.39	424
	1000	5.2	0.42	0.15	0.10	100
Oahu	444	6.3	1.18	0.32	0.22	33
	750	5.8	0.88	0.15	0.22	23
Maui	621	5.9	0.88	0.16	0.14	25
	714	6.3	0.98	0.17	0.15	17

*This soil had received a heavy lime application.

†These soils had received an application of molasses ash which contains considerable potassium carbonate.

and sulfate as well as easily soluble silicates. These facts point strongly toward a definite influence which lime exerts over the availibility of phosphates in soils high in iron and aluminum. This is further indicated by the high P_2O_5 content of juice from cane grown on the high lime soils.

<div align="center">DISCUSSION</div>

Our studies on Hawaiian soils have shown the large amounts of aluminum phosphate which are present and lesser amounts of iron and calcium phosphates in the order given. These studies further show that where an excess of lime is present, for example the coral interspersed areas, the percentage of phosphate combined with aluminum and iron is low and that the availability and assimilation by the cane is high, in spite of the fact that there is little consistent difference in the iron and aluminum content of the two types. On the other hand the analyses of upland soils show a lower lime content, higher acidity, lower availability and larger quantities of soluble or active aluminum.   .

The normal phosphates of iron and aluminum have been shown to give response on Hawaiian soils deficient in this form of plant food (5). This suggests the association of basic phosphates with the low availability of phosphates in island types.

The availability of phosphates in the virgin soils of these islands is notably increased by cultivation and other tillage practices. It is possible to explain this on the basis of a stimulation of the buffer action of $CaHCO_3$ through the introduction of carbon dioxide into the soil atmosphere by aeration. The carbon dioxide precipitates the elements which stand higher in the electromotive series and whose basic phosphates are less easily attacked by the agents of solution.

Again the subsoils of these islands are notably lower in available phosphates than the corresponding top soil. Here also we have a lower lime content, less aeration and higher acidity. There results from the above environment an excess of the phosphates of iron and aluminum both normal and hydrated as shown by our soil analyses.

The work of Walker (9) illustrates these principles. These investigators, in their examination of the phosphate content of the juice from a number of fields at Pioneer Plantation on the Island of Maui, found that the juices from cane grown in the lower elevations were richest in P_2O_5. Cane juice produced at an elevation of 500 feet contained slightly less P_2O_5 and at the highest elevations, the least P_2O_5. This plantation is so situated that there is a gradual slope up the mountain to an altitude of 1500 feet. Messrs. Stewart and Hansson, of this station, have recently completed a soil survey of this plantation. Their analyses have been separated as to altitude, averaged and are shown here:

Relations of altitude, soil reaction, and soil composition to P_2O_5 in cane juice

ALTITUDE	REACTION	CaO SOLUBLE IN CONCEN-TRATED HCl	CaO SOLUBLE IN 1 PER CENT CITRIC ACID	TOTAL P_2O_5 CONTENT	P_2O_5 SOLUBLE IN 1 PER CENT CITRIC ACID	SiO_2 SOLUBLE IN 1 PER CENT CITRIC ACID	P_2O_5 IN JUICE*
feet	*pH*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
100	7.9	3.23	0.39	0.37	0.0320	0.23	0.063
200	7.3	0.40	0.22	0.34	0.0064	0.17 ⎫	0.024
300	7.2	0.46	0.20	0.27	0.0044	0.18 ⎭	
400	6.7	0.33	0.17	0.32	0.0045	0.13	
500	6.6	0.28	0.16	0.32	0.0039	0.14	
700	6.2	0.31	0.15	0.26	0.0042	0.12 ⎫	
800	6.0	0.22	0.11	0.26	0.0026	0.09 ⎬	0.013
1000	6.5	0.25	0.14	0.36	0.0027	0.10 ⎭	

*As found by Walker (9).

These results show very clearly the relation of these factors to the assimilation of phosphoric acid by the cane and indicate the practical possibilities of their application. There is practically no difference in the total P_2O_5 content of the soils at any altitude, the average at 1000 feet being practically as high as at 100. Total lime decreases slightly with altitude which is true of all Hawaiian soils on the mountain slopes. Available silica and phosphoric acid as measured by 1 per cent citric acid solution shows a remarkably consistent relation to assimilation.

SUMMARY

1. There is a definite relation between the availability of silica and phosphoric acid in Hawaiian soils as measured by the response of sugar cane to phosphate manuring.

2. The reaction of the soil and the forms of lime present are also closely related to the availability of phosphoric acid.

3. The applications of these theories to field conditions is shown by the relation of acidity and solubility of silica and lime to the P_2O_5 content of cane juice from cane at Pioneer Plantation.

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A STATISTICAL STUDY OF THE DISTRIBUTION OF SOIL MATERIAL IN THE UNITED STATES ACCORDING TO THE SIZE OF ITS PARTICLES

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Comparisons are frequently made of the extent of particular soil classes in different regions. Such comparisons are of distinct value but fail to give a definite picture of the size-distribution of soil material since any soil class is composed of particles of varying sizes.

If the area of a soil class is multiplied by the percentages of each of its separates, determined by mechanical analysis, the result is the areas of the separates. If this is repeated with each soil class and the areas of like separates summed, the total area represented by the various classes will then be reduced to the areas of the separates. The area of each separate divided by the total area of all the classes will then give the ratios of the areas of the separates to the total area. This may be stated with greater clearness by using the following algebraic equations:

If $X_1, X_2, \ldots X_n$ = areas of soil classes in any locality of Area "A,"

And if $a_1, a_2, \ldots a_n$ = percentage of separate 1 (the coarsest separate in the mechanical analysis) in each soil class,

And $b_1, b_2, \ldots b_n$ = the percentage of separate 2;

Then $X_1a_1 + X_2a_2 + \ldots + X_na_n = A_1$

And $X_1b_1 + X_2b_2 + \ldots + X_nb_n = B_1$

Where A_1, B_1 = areas of separates 1 and 2, respectively.

The ratios A_1/A, B_1/A will furnish points on the size-distribution curve, and by continuing the process for each soil class of a given locality the entire area may be represented by a size-distribution curve.

The number of equations and therefore the number of points on the curve will be equal to the number of separations made in the analysis, while the number of soil classes in the area will give the value of n. If five separations are made in the analysis of each of five soil classes, we will have the following five equations:

$$X_1a_1 + X_2a_2 + X_3a_3 + X_4a_4 + X_5a_5 = A_1$$
$$X_1b_1 + X_2b_2 + X_3b_3 + X_4b_4 + X_5b_5 = B_1$$
$$X_1c_1 + X_2c_2 + X_3c_3 + X_4c_4 + X_5c_5 = C_1$$
$$X_1d_1 + X_2d_2 + X_3d_3 + X_4d_4 + X_5d_5 = D_1$$
$$X_1e_1 + X_2e_2 + X_3e_3 + X_4e_4 + X_5e_5 = E_1$$

The order of procedure, which is entirely arbitrary, is from the coarser to the finer material both in soil class and soil separate. The five equations will completely resolve any area into its component parts. It is to be understood that the average mechanical analysis of a soil class will define that class. It should be emphasized at this point that these equations are general and will apply to any area where the soils have been classified and the method of analysis is known.

When the soils of the United States are considered, it is evident that the method of analysis of the United States Bureau of Soils should be used, and seven equations will then be required.

Since it is physically impossible to differentiate a large number of classes in any area the value of n will be small. Values for the a's, b's, c's, d's, e's, f's, and g's may be found by averaging a large number of analyses of the various classes. Such averages, however, have been made by Whitney (5), and his result have been used in the calculations of this article. It is evident in table 1, page 12 of this bulletin, that 8664 soils distributed in eleven classes have been used to arrive at the average percentages of the classes. The reliability of these averages is confirmed by several hundred additional analyses of the different classes, which failed to show appreciable changes. It should be noted, however, that Whitney's data have been rounded off and that this process has introduced a relatively greater error in the coarser separates.

Each of the thirteen soil divisions outlined by Marbut and associates (3) has been treated by this method. Table 1 is a summary of the areas of the soil classes of the thirteen divisions. Table 2 is derived from table 1 by applying the seven equations to the soil classes in each division as indicated above.

The seven ratios A_1/A, B_1/A, ... G_1/A, as percentages, for each of the thirteen soil divisions, together with their averages, are shown in figure 1 as histograms. Diameters are plotted as abscissa on a logarithmic scale, while the percentage of a separate is represented as an area between its size limits. The value of a particular ordinate is therefore the quotient obtained by dividing the percentage by the number of unit spaces of abscissa defining the separate. The total area under a histogram is 100 per cent.

The data in figure 1 are given in two charts for the sake of clearness, the curve of the average being shown in both to facilitate comparison. The lower limit of clay has been arbitrarily fixed at 50 $\mu\mu$. This is probably justified by recent studies of colloidal material in soils. It is clear, however, that a different lower limit would necessitate a corresponding change in the value of the ordinate of this separate.

Since the curves are weighted by the areas of the various classes, the curve of the mean will also represent the average soil class, which approximates closely a loam; and since the classes of table 1 are representative of a very large number of areas and a very large total area it is not unlikely that the average soil in the United States is a loam. The ratios for the average, as given in table 2, will be designated the "general mean."

TABLE 1

Areas of individual soil classes for the thirteen Soil Divisions of the United States*

PROVINCE OR REGION	COARSE SAND	SAND	FINE SAND	SANDY LOAMS	FINE SANDY LOAMS	LOAMS	SILT LOAMS	CLAY LOAMS	SILTY CLAY LOAMS	CLAY	TOTAL AREA OF SOIL CLASSES
	acres	acres	acres	acres	acres	acres	acres	acres	acres	acres	acres
Atlantic and Gulf Coastal Plain	548,738	4,681,278	6,108,270	7,681,334	19,603,248	5,039,296	2,284,562	2,939,552	433,152	6,744,830	56,064,260
Appalachian Mountain and Plateau	....	309,766	....	1,086,829	1,005,696	4,243,868	2,339,584	2,728,144	452,352	751,837	12,918,076
Piedmont Plateau	3,904	6,784	....	4,531,214	674,304	2,577,093	548,212	975,722	....	2,667,241	11,984,474
Glacial and Loessial	....	1,262,536	409,356	1,401,140	1,053,504	6,973,008	13,830,720	3,657,690	17,856	....	28,605,804
Glacial, Lake, and River Terrace	147,848	778,032	607,102	1,557,944	904,462	2,012,620	604,474	794,240	138,432	1,632,060	9,177,214
Limestone Valleys and Uplands	....	....	....	83,526	9,536	5,284,992	2,318,146	604,660	78,784	532,226	8,911,870
Great Plains	....	1,003,072	1,264,064	1,758,784	7,869,773	6,760,365	28,968,679	8,441,984	....	1,460,608	57,527,329
River, Flood, Plains	8,000	131,072	277,568	323,291	1,884,096	1,943,673	4,069,449	250,944	1,203,968	4,895,335	14,987,396
Rocky Mountains	....	136,960	3,008	284,480	209,664	87,232	159,872	92,992	9,664	135,872	1,119,744
Great Basin	....	38,100	34,168	238,716	229,516	219,318	....	282,090	....	25,600	1,067,508
Arid Southwest	....	168,192	67,074	217,128	158,428	209,870	24,320	426,193	....	64,663	1,335,868
Northwestern Intermountain	....	180,928	189,642	81,216	702,748	465,606	414,086	15,680	....	15,552	2,065,460
Pacific Coast	77,312	1,442,762	207,746	3,254,416	1,437,378	2,693,208	1,001,081	1,374,537	1,911,168	1,543,356	14,942,964
Grand Total											220,707,967

* Reference to Marbut, et al. (3) will show that the areas in this table correspond to the areas upon which soil types have been definitely established.

TABLE 2

Acreage of the seven separates (values of $A_1, B_1, C_1, D_1, E_1, F_1,$ and G_1) in each of the thirteen soil divisions of the United States.

SOIL DIVISIONS	SEPARATES						
	1	2	3	4	5	6	7
	acres	acres	acres	acres	acres	acres	acres
Atlantic and Gulf Coastal Plain........	994,318	3,329,548	4,029,202	15,355,480	9,349,655	14,421,615	8,634,353
Appalachian Mountains and Plateau.....	202,799	617,637	606,169	1,921,884	1,842,011	5,292,852	2,434,725
Piedmont Plateau....................	282,049	870,380	799,730	2,115,827	1,590,504	3,832,292	2,493,692
Glacial and Loessial.................	410,269	1,191,437	1,175,039	3,638,155	3,826,998	13,844,096	4,519,810
Glacial Lake and River Terrace........	181,296	612,709	663,351	1,921,816	1,269,409	2,823,300	1,705,333
Limestone Valleys and Uplands........	143,687	363,486	333,454	1,062,971	1,293,291	4,110,051	1,604,931
Great Plains.......................	705,672	1,880,228	1,708,715	7,388,792	7,739,480	28,697,388	9,407,055
River Flood Plains..................	169,161	491,344	431,444	1,861,985	1,842,886	6,563,950	3,626,626
Rocky Mountains....................	21,877	79,485	86,820	235,956	158,929	348,813	187,864
Great Basin........................	20,411	68,018	72,768	241,135	172,120	314,410	178,646
Arid Southwest.....................	23,653	90,859	106,862	302,979	195,084	385,076	231,355
Northwestern Intermountain..........	29,556	99,021	126,793	514,208	359,344	678,611	257,927
Pacific Coast......................	277,815	1,009,074	1,064,965	2,787,650	1,970,609	5,121,076	2,711,785
Totals..........................	3,412,561	10,703,225	11,205,402	39,348,836	31,610,320	86,433,531	37,994,101
Percentage of total area............	1.54	4.85	5.08	17.83	14.32	39.16	17.22
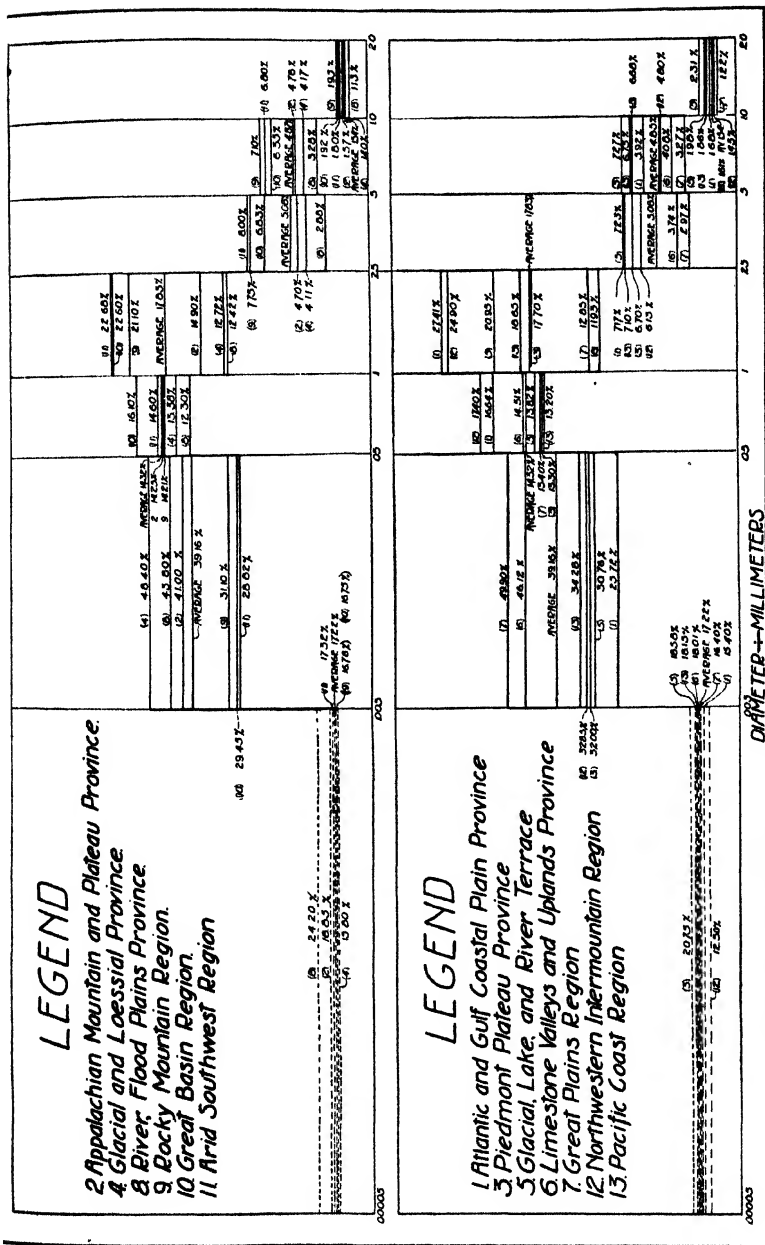
Fig. 1. Size Distribution Curves for Thirteen Soil Provinces

The percentage of each separate is represented by an area between its limiting diameters, which are plotted on a logarithmic scale for convenience. The total area under each curve is equal to 100 per cent.

An examination of Whitney's mechanical analysis data of the common soil classes (5) shows that there is a smaller range of variations for separate 5 than for any other separate except 1. This condition is nearly maintained when the data are weighted by the areas of soil classes in a region, as is shown by the tendency of the histograms to converge in separate 5. This convergence is a striking feature of the distribution curves and suggests that the soil classes are distributed in such a way that the ratio E_1/A approaches constancy. Four of the thirteen divisions show deviations from the "mean" (14.32 per cent) of 3.0 to 1.5 per cent, while in the remainder the same deviation is from 1.1 to 0.1 per cent. It should be noted that two of the four more divergent divisions are soil regions of the West where relatively small areas had been surveyed previous to 1912, and further that of the area surveyed at this time a high percentage had been done at an early period in the organization of the soil survey, when the differentiation between soil classes was less definite. Thus, in the Great Basin 80 per cent of the total acreage used to obtain the

TABLE 3

Statistical criteria for the thirteen soil divisions

	SEPARATE NUMBERS						
	1	2	3	4	5	6	7
Percentage ranges (taken direct from figure 1)............................	1.18	4.0	5.1	15.5	5.1	24.2	11.7
Standard deviations......	0.04	0.28	0.38	3.94	0.58	6.1	1.28
Probable errors......................	0.03	0.19	0.29	1.95	0.39	4.1	0.86
Coefficients of variability..........:..	0.03	0.06	0.09	0.16	0.04	0.16	0.08

histogram of that region had been reported by 1904 (3). The River Flood Plain and the Atlantic and Gulf Coastal Plain Provinces are the two other divisions showing maximum deviations at separate 5. It is well-known that many of the soils of these provinces have been affected by sorting agents which might be expected to yield anomalous results as will be brought out later.

The standard deviation $\sigma = \sqrt{\dfrac{\Sigma \chi^2 f}{N}}$ for the thirteen divisions has been calculated for each of the seven separates. In this formula $\Sigma \chi^2$ is the sum of the squares of the deviations from the "general mean," N is the total area in acres of all the soil divisions, and f is the number of acres of a particular separate.

The percentage range, the probable errors ($0.6745 \times \sigma$) and the coefficients of variability for the data in figure 1 are given in table 3. The coefficient of variability is the quotient $\dfrac{\sigma}{m}$ where m is the "general mean" percentage of the separate.

The percentage range, standard deviations, and probable errors are greater for E_1/A(separate 5) than for the same function in the case of any of the first three separates. The coefficients of variability shows, however, that this is due to the smaller acreage of the coarser separate. The standard deviations are shown graphically in figure 2. In the heavy, unbroken curve they have been plotted directly as ordinates, while in the broken line each value of σ is distributed between its size limits by dividing by the number of unit spaces included in its segment of abscissa.

To determine to what extent smaller areas deviate from the "general mean," the individual areas for which detailed survey studies are recorded in the Annual Progress Report of the United States Bureau of Soils for the years 1913–1916, inclusive, were summarized as to soil class and treated by the seven equations. The ratios A_1/A, B_1/A, ... G_1/A were then calculated and compared with the "general mean." These ratios were worked out for 229 areas representing nearly 90,000,000 acres and distributed between thirty-two states. The distribution of the deviations from the "general mean" is shown graphically in figures 3 and 4. The ordinates represent the percentage of the 229 areas having deviations within the range given by the abscissa. The numbers on the curve correspond to the numbers of the separate.

The probable errors for these deviations, calculated from the formula

$$\text{P.E.} = 0.6745 \sqrt{\frac{\Sigma x^2}{N-1}}$$

are as follows:

SEPARATES						
1	2	3	4	5	6	7
0.45	1.82	2.39	6.82	2.17	10.82	2.95

In the formula Σx^2 is the sum of the squares of the deviations from the "general mean," and N is the number of areas considered.

It will be seen that even for small areas the deviations in separate 5 are very much less than in separates 4, 6, and 7, in spite of the fact that the probable errors for small areas are considerably greater than for large areas, as may be seen by comparing these values with the probable errors of table 3. Thus, to take a specific example, the percentage of the areas having deviations within 2 per cent of the "general mean" are as follows:

SEPARATES						
1	2	3	4	5	6	7
98	55	42	15	49	10	36
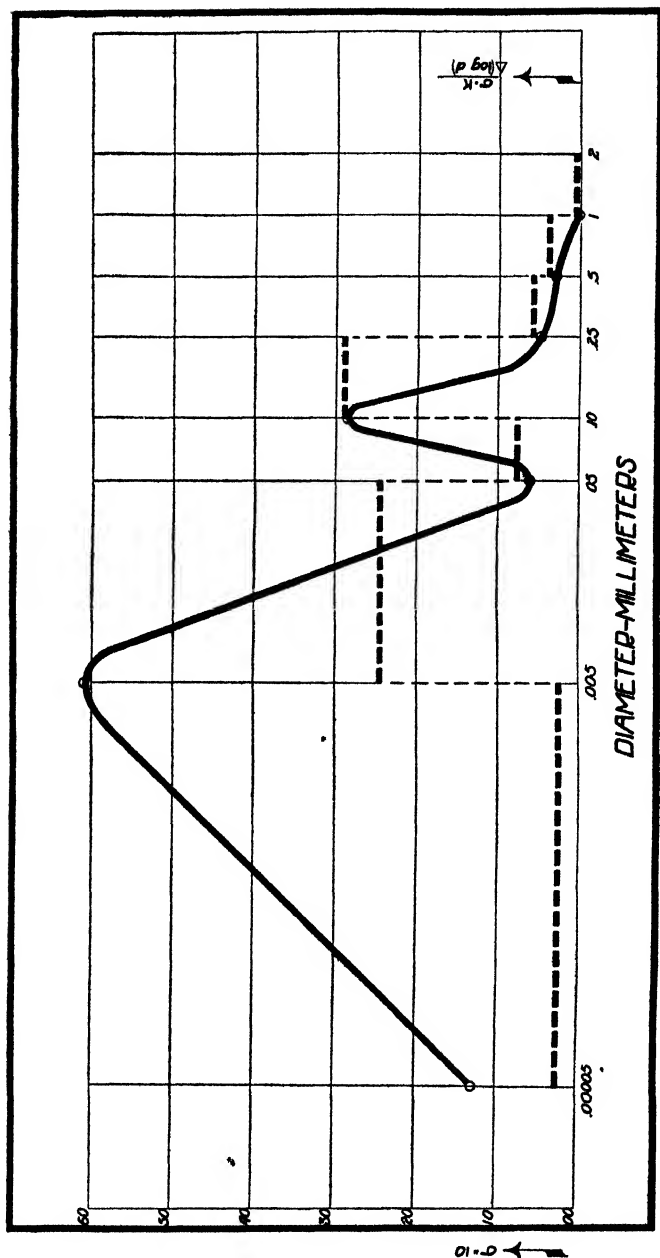
Fig. 2. Standard Deviations for the Seven Separates

The abscissa, along which diameters are represented, is divided into seven segments. Standard deviations σ are shown as ordinates in both curves. In the unbroken curve σ for each segment is plotted a point at the smaller end of the segment. In the broken curve, each σ is divided by the number of unit spaces in each segment. The ordinate is $\dfrac{\sigma}{\Delta \log d}$ (K) where K = 100.
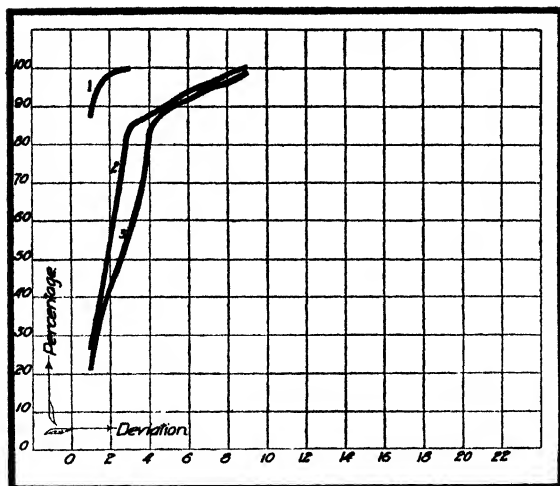
FIG. 3. DEVIATIONS FROM "GENERAL MEAN" FOR SEPARATES 1, 2 AND 3

The ordinates represent the percentage of the 229 areas having deviations from the "general mean" within the range given by the abscissae. The numbers on the curves correspond to the numbers of the separates.
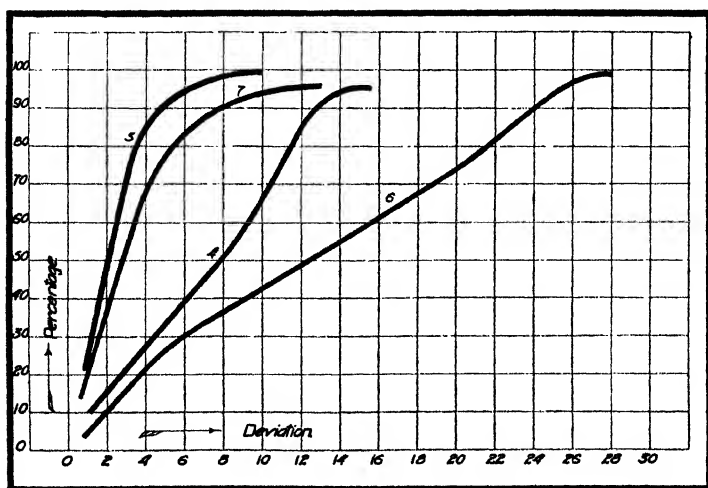
FIG. 4. DEVIATIONS FROM GENERAL MEAN FOR SEPARATES 4, 5, 6 AND 7

The ordinates represent the percentage of the 229 areas having deviations from the "general mean" within the range given by the abscissae. The numbers on the curves correspond to the numbers of the separates.

Further confirmation of the approximate constancy of the percentage of separate 5 may be found by examining the analysis of Whitney's average soil classes (5), as presented in figure 5. The ordinate shows the percentage of material of smaller diameter than the value of the corresponding abscissa. The curves take the general form of an "S," and separate 5 lies between the
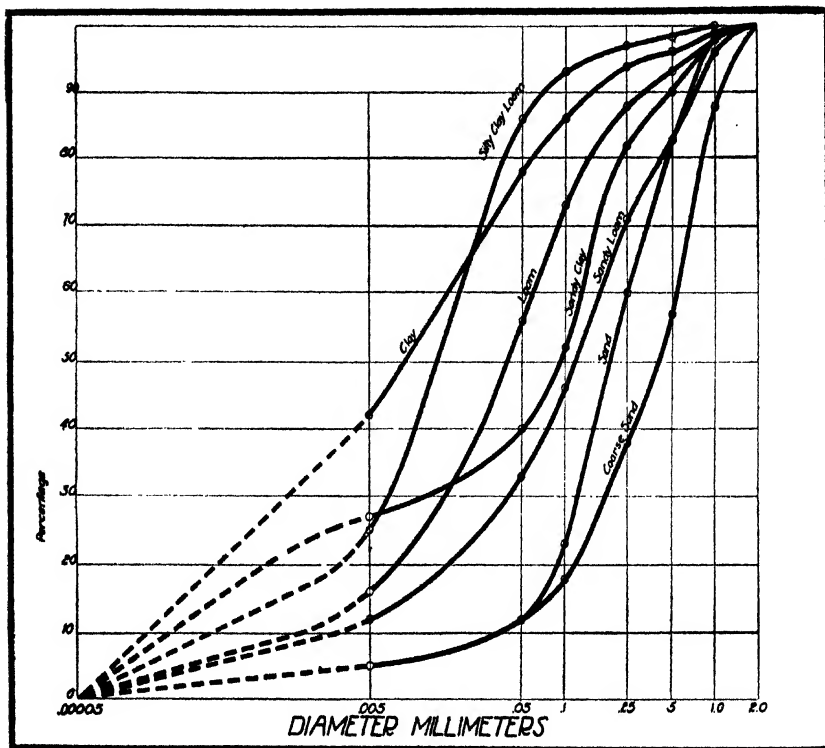
FIG. 5. AVERAGE COMPOSITION OF SOIL MATERIAL AS ANALYZED IN CONNECTION WITH THE SOIL SURVEY

The ordinates represent the percentages of material of smaller diameter than the value given by the corresponding abscissae. Merely to avoid confusion, four soil classes have been omitted, but these types are similar to others shown on the chart. *Data for this figure were taken from table 1 by Whitney (5, p. 12).*

regions of maximum curvature. In coarse-textured soils, separate 5 is nearer the lower bend, and in fine-textured soils near the upper bend, while in soils of intermediate texture it falls near the point of inflection. It will be observed that the segment of the curves representing separate 5 are nearly parallel for all the common soil classes and therefore that the condition that E/A is nearly

constant can be predicted.   On the other hand, the segments for separate 4 are nearly horizontal for fine-textured soils and nearly vertical for coarse-textured soils, while the opposite is true for separate 6.   Accordingly, it is to be expected that the large variations for different soil classes will be found in these separates.

The chart also indicates that the limit for separate 5 could be extended without materially affecting the ratio of E/A.   To establish this rigorously would require a method of analysis giving more data in this region.   The value of ascertaining whether the marked variations found in separates 4 and 6 apply over the entire range of these separates is evident, since the region of marked variation would then be located more definitely.

The mode in the histograms of figure 1 usually occurs immediately above or below separate 5.   A majority of the soils will be coarse- or fine-textured, depending upon whether the mode is in separate 4 or 6, respectively.   In case the ordinates are approximately the same for separates 4, 5, and 6, the soil-class distribution will be about equal between fine- and coarse-textured soils, or in other words will approximate loams.   This is confirmed by table 1 and also by the table given by Marbut and associates (3, p. 9) which shows the percentage of distribution of the different soil classes in the several provinces.

It appears, therefore, that there are two extreme types of soil material, one of which weathers to give a maximum ordinate in separate 4, while the other breaks down to a finer state with a mode in separate 6.   The explanation of this fact that seems most plausible to the writer is that the relatively hard minerals with poor cleavage remain in the coarser separates and apparently tend toward a mode in separate 4, whereas those minerals which are relatively soft and possess good cleavage go into the finer separates and tend to reach a maximum.

A statement of McCaughey and Fry (4) in this connection is interesting. They say that "certain generalities have been established regarding the composition of these 'mechanical separates' of a soil.   Quartz predominates in the coarser separates, while as the diameter decreases there is present in increasing proportions fragments of the softer minerals and those possessing good cleavage, such as kaolinite, the feldspars, etc.   It is probably from *a priori* considerations and fro n chemical analyses that the clay separate is richest in such minerals, but this cannot now be definitely proved.   On the other hand, ferric hydroxide, alumina, and kaolin also tend to accumulate in the clay."

It is true that quartz predominates in the coarser separates in many soils, and perhaps in most soils, yet there must be important exceptions.   The recent work of Hendrick and Newlands (1) shows two important Scottish soil types of thin "glacial drift" origin to be very low in quartz in all the separates examined.   The soils were derived from basic igneous rock of the olivine-gabbro type and in the coarse separates carried high percentages of mineral of the orthoclase group (mainly orthoclase and microcline).   In other

soils derived from rocks of the syenite type, and even from the granitic type, the coarser separates contained high percentages of the orthoclase group. The quantitative phase of this work was not carried far enough into the fine separates to indicate whether or not there might be a relation between the distribution of the minerals and the size of particles.

The fact that the parent rock is so commonly a mixture of a number of varieties of mineral makes definite proof of the above explanation difficult and in reality a problem in statistics. It is possible, however, that definite tendencies might be indicated by tabulating the distribution of the separates of a number of soil series derived from certain rock types. It is obvious that only residual soils should be used in this connection in order to eliminate as far as possible the action of sorting processes. Table 4 gives the ordinates of the seven separates for a number of important soil series as reported by the United States Bureau of Soils, taking into account all the recorded soil types of each series (3). The ordinates have been calculated as indicated above and described in figure 1. The percentage of the separates may be found from the ordinates by multiplying the ordinates by the following factors which represent the relative distances of abscissa on a logarithmic scale between the limits of the separate.

SEPARATES						
1	2	2	4	5	6	7
3	3	3	4	3	10	20

Table 4 shows that the limestone and slate soils are above the "general mean" in separate 6 and considerably below in separate 4. This condition is reversed in the case of the soils derived from igneous rocks. Soils coming from a mixture of sandstone and shale, on the other hand, give ordinates which are nearly average though tending toward the limestone type of distribution. In this case the shale might be expected to give a high value in separate 6 and the sandstone a high value in separate 4, and the resultant soil to be near an average. It is possible in this case that the shale somewhat predominates, although this cannot be definitely proven.

The Cecil, Durham, and Appling series which are derived from quartz-bearing igneous rocks are considerably above the "general mean" in fine gravel, coarse sand, and medium sand, while the limestone and slate soils are low in these separates.

The data of table 4 indicate in a general way that it might be possible to predict the location of the mode in a histogram of a residual soil area from a knowledge of the parent rock. Before any such application could be made to transported soils the extent of the sorting of the separate by the transporting agents must be known in addition to the rock types. In both cases the maturity of the soil, and perhaps the climate of the region, must be taken into

account.   Obviously histograms for soil areas of known rock derivation must first be worked out as a basis for the analogy.   This is a task requiring considerable effort.   However, it was felt that central tendencies might be indicated by calculating the percentages of the different parent rock-types for a number of the histograms of figure 1.   Table 5 is such a calculation based on the rock data given by the United States Bureau of Soils.

In this table the rock types have been divided into four divisions based upon the tendencies to disintegrate into size limits, as indicated in table 4.

TABLE 4

*Ordinates of the seven separates and the kind of rock from which the soil is derived for some of the important residual soils of the United States**

SOIL SERIES	DERIVED FROM	HEIGHTS OF ORDINATES IN SEPARATES						
		1	2	3	4	5	6	7
Alamance	Carolina slates	0.37	0.81	0.54	1.73	3.96	6.06	0.78
Georgeville	Carolina slates	0.35	0.84	0.62	1.87	3.91	5.79	0.87
Crawford	Limestone (pure)	0.39	1.01	0.75	2.13	3.52	4.68	1.37
Colbert	Limestone	0.28	0.80	0.58	2.32	3.95	5.42	0.99
Decatur	Mainly pure hard limestone	0.42	1.34	1.24	3.14	4.62	4.32	1.07
Clarksville	Limestone (cherty) St. Louis to Lower Carboniferous	0.56	1.26	1.22	2.91	4.97	4.82	0.79
Hagerstown	Limestone (mainly pure) Cambro-Silurian Age	0.52	1.33	1.21	2.96	4.65	4.52	0.99
De Kalb	Sandstone and shale (Silurian to Carboniferous)	0.55	1.58	1.50	3.20	4.52	4.67	0.81
Upshur	Sandstone and shale (usually of calcareous nature)	0.54	1.54	1.52	3.92	5.17	4.00	0.92
Iridell	Mainly diorite, hornblende schist, or hornblende gneiss and chloritic rocks	0.48	1.61	1.60	5.05	5.22	3.20	1 06
Cecil	Granite and gneiss	0.81	2.63	2.41	4.60	4.16	2.94	1.14
Durham	Granite and gneiss (rather coarse-grained)	1.22	4.04	3.79	6.40	4.60	2.15	0.60
Appling	Grey schist, hornblende schist, gneiss	1.27	4.08	3.79	6.22	4.50	2.21	0.61
Average for soils of United States as shown in fig. 1 ...		0.51	1.62	1.69	4.46	4.63	3.92	0.87

* Any ordinate in separates 1, 2, 3, and 5 may be converted to a percentage of the area of the series by multiplying that ordinate by 3; and the ordinates in 4, 6, and 7 by 4, 10, and 20, respectively.

These divisions are as follows: Those that yield a product (1) high in sand and clay but low in silt, (2) approximately average in distribution, (3) high in silt, low in sand, and nearly average in clay, and (4) reworked material whose distribution will depend upon the nature of the sorting agent.

The three bottom rows of figures in table 5 are taken from figure 1.   The first two rows give comparisons of the heights of the ordinates using the height of the "general mean" as standard, while the third gives the location of the mode in the histogram.   The figures in the main body of the table show the

TABLE 5

Qualitative relation between certain rock types and the content of sands, silt, and clay in the soils derived from them*.

ROCK TYPE	PROVINCES								PRINCIPAL MECHANICAL DIVISIONS
	Piedmont	Appalachian	Limestone Valleys	Glacial and Loessial	Great Plains	Pacific Coast	Atlantic and Gulf Coastal	River Flood Plains	
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	
Granite and gneiss with some schist	72.0	12.8	....	5.3	13.1	17.3	....	....	Sands and clay high, low silt content.
Mainly schist	14.0	1.4	....	....	....	14.9	....	....	
Diorite and diabase	5.2	....	....	....	....	....	....	....	
Sandstone and shale	7.1	77.5	....	....	13.8†	20.5	....	....	Nearly an average distribution
Granite, shale, limestone, and sandstone	....	....	....	41.6	15.2	....	....	....	
Sandstone, shale, limestone, and crystalline	....	....	....	....	....	20.0	....	....	
Sandstone, shale, and limestone	....	6.0	4.3	2.9	10.5†	....	....	....	High silt content
Shale and limestone	....	....	....	8.6	12.2	....	....	....	
Limestone	....	....	95.6	....	....	....	26.0	....	
Loessial material	....	....	....	39.2	32.6	....	2.9	36.3	
Glacial	....	....	....	....	....	26.0	....	3.0	
Reworked residual prairie material	....	....	....	....	....	....	13.7	20.5	
Reworked piedmont appalachian material	....	....	....	....	....	....	57.3	5.5	
Reworked coastal plain material	....	....	....	....	....	....	....	25.5	
Reworked applachian and limestone valleys material	....	....	....	....	....	....	....	9.2	
Miscellaneous	1.8	2.2	....	....	2.6	1.3	....	....	
Separates with ordinates:									
(1) Above average	1–3,7	1,6,7	1,5–7	6	6	1–4,7	1–5	6,7	
(2) Below average	4,5,6	2–5	2–4	1–5,7	1–5,7	5,6	6,7	1–5	
Mode or maximum ordinate	4	5	5,6	6	6	4	4	6	

* The figures in the main body of the table are the percentages of each soil division that has been derived from the different rock types. The percentages are based upon the areas of table 1.

† Soil area, often calcareous.

percentages of each soil division which has been derived from the different rock types.

The table shows that 86 per cent of the Piedmont area, 78 per cent of the Appalachian area, and 100 per cent of the Limestone Valleys area are derived from the rock types of divisions (1), (2), and (3), respectively. Further, it will be seen that the mode is in separate 4 in the Piedmont Plateau, that it is in separate 5 in the Appalachian Mountains and Plateau, and in the Limestone Valleys and Uplands it is in separates 5 and 6. The presence of the mode in separate 5 may not represent the actual distribution. The mechanical analysis data are insufficient for the construction of continuous curves, and the exact location of the mode is not definite. If, however, the curves are smoothed the modes will be shifted towards the left, since the space representing separate 6 is over three times that representing separate 5. This smoothing can best be accomplished by plotting the data as ogives, as illustrated in figure 5. The points of maximum slope on the ogives will give the location of the modes. By this procedure the mode in the Limestone Valleys will be found at approximtely 0.02 mm. diameter and at about 0.04 mm. diameter in the Appalachian.

It is evident that the above location of the mode depends upon the method of plotting the data on a logarithmic scale. If an arithmetic scale were used the mode in all cases of figure 1 would be shifted into the clay. In a previous publication (2) it was shown that if the weight of particles of radius r is plotted as a continuous function of (1) the radius and (2) the logarithm of the radius the relation between corresponding ordinates is given by the expression $W_1 = W_2 \div r$, where W_1 and W_2 are the ordinates associated with unit area under the W_1r and $W_1\log r$ curves, respectively.

It can readily be shown that whereas the condition for the mode on the arithmetic scale is $dw/dr = 0$, on the logarithmic scale this condition is $dw/dr = w \div r$. The two modes are therefore not coincident. The selection of the logarithmic scale has been made because of its convenience. However, the $w_1\log r$ curve may characterize the soil quite as well as the w_1r curve.

The histograms for the Glacial and Loessial Province and the Great Plains Province are nearly identical. It will be noted that the percentages of the areas of these provinces falling in the three divisions of rock-types do not differ greatly. Thus, 50.7 per cent of the Glacial and Loessial and 55.3 per cent of the Great Plains Area are derived from rock-types of division (3), while the percentages of the areas derived from rock-types of division (2) are 42 for Glacial and Loessial and 29 for the Great Plains. In both of these regions the mode is in separate 6 as is also the mode for the River-Floods-Plain Province. In each of these three divisions a third or more of the area of each is loessial material which is an important factor in giving a high silt content to the area.

The rock-types in division (1) furnish 32 per cent of the soil area of the Pacific Coast region, while those of division (2) furnish 40 per cent. The

mode of this region is in separate 4. Twenty-six per cent of this area is glacial material of unknown derivation. However, judging from the shape of the histogram this 26 per cent would probably be quartz-bearing igneous rock.

The soils of the River-Flood Plain and the Atlantic and Gulf Coastal Plain are largely re-worked material. In the former (see table 1) 70 per cent of the soil is finer in texture than loam, while in the latter (see table 1) 68 per cent is coarser-textured than loam. Sorting of the separates has been carried to an extent that makes distribution studies untrustworthy, but general tendencies might be indicated. The spreading of a stream over its flood plain is accompanied by a deposition of silt and clay, while wave action tends to remove the fine material.

SUMMARY

Histograms representing the average textural composition of the thirteen soil divisions of the United States have been worked out from the data of Bulletin 96 of the United States Bureau of Soils (3).

It was found that the ratio of the area of separate 5 to the total area is approximately constant, for the thirteen divisions. This ratio, expressed as a percentage, is 14.32 ± 0.39. The standard deviation and probable errors are less for separate 5 than for separates 4, 6, and 7, while the coefficient of variability is less for separate 5 than for any other separate except 1. The same relative condition with respect to separate 5 maintains for 229 smaller areas well distributed throughout the United States.

Each histogram was characterized by a mode in either separates 4 or 6 and the constancy of separate 5 is explained on this basis. In order to explain the position of the mode the distribution of the soil from several parent rock-types was studied. It was shown: (1) that quartz-bearing igneous rocks tend to give soils low in silt and high in sand and clay, (2) soils whose parent rock are mixtures of sandstone and shale approximate the average texture, and (3) limestone, slate, shale, and loessial material tend to give soils of high silt and low sand content.

These criteria have been applied to eight of the thirteen soil divisions and offer an explanation of the distribution of soil classes. Sufficient geological and pedological data are not at hand to treat the other five divisions.

It was also shown that the "general mean" which probably represents the average soil class of the United States, is a loam.

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THE ACTION OF DICYANDIAMID AND GUANYL UREA SULFATE ON PLANT GROWTH[1]

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INTRODUCTION

In the latter part of the nineteenth century, leaders in agriculture realized that the production of a sufficient supply of nitrogenous fertilizers was becoming a serious problem. It was evident that the problem of meeting the deficiency of nitrogen caused by the removal of crops must find its solution in the vast stores of nitrogen in the atmosphere. In 1895, Frank and Caro succeeded in developing a process by which nitrogen is fixed in a form readily utilized by plants. The new fertilizer, calcium cyanamid, was immediately investigated and was found to be a good substitute for the older nitrogenous fertilizers. However, it was generally observed that its fertilizing value deteriorated greatly in storage, and the probable cause of this was found in the fact that cyanamid readily polymerizes into dicyandiamid as first shown by Beilstein and Gauther in 1862.

More recently new nitrogenous fertilizers are being exploited, among them synthetic urea. During the process of manufacture of urea from calcium cyanamid a small quantity of cyanamid polymerizes into dicyandiamid which, in the presence of sulfuric acid, takes up a molecule of water to form the strongly alkaline dicyandiamidin. This combines with the sulfuric acid to give dicyandiamidin sulfate, more commonly known as guanyl urea sulfate. The reactions may be represented as follows:

$$2CH_2N_2 \rightleftarrows C_2H_4N_4$$
$$\text{Cyanamid} \qquad \text{Dicyandiamid}$$

$$C_2H_4N_4 + H_2O \rightleftarrows C_2H_6N_4O$$
$$\text{Dicyandiamid} \qquad \text{Dicyandiamidin}$$

$$2C_2H_6N_4O + H_2SO_4 + 2H_2O \rightleftarrows (C_2H_6N_4O)_2 \cdot H_2SO_4 \cdot 2H_2O$$
$$\text{Dicyandiamidin} \qquad \text{Dicyandiamidin sulfate}$$
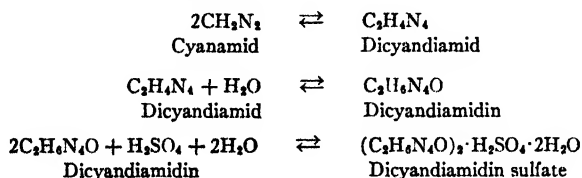
These impurities constitute from 1 to 10 per cent of crude urea, and it is essential that we know to what extent they lessen its fertilizing value.

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Most of the investigations with dicyandiamid and its salts have been carried on in the European countries where the necessity of using calcium cyanamid was more urgent. Since the work of Gerlach (4) and Wagner and Gerlach (5), who first discovered the toxic effects of dicyandiamid, several men have touched upon this subject in connection with their cyanamid investigations but have left meager and contradictory information.

Seelhorst and Müther (30) were the first to give any definite information regarding the action of this compound. They found that in sand it killed the young plants, while in loam soil the plants grew normally except for the drying of the leaf tips, an injury which following investigators have found to be characteristic. Sjollema and Ruijter de Wildt (31) showed that dicyandiamid had no injurious influence on germination, but caused later ill effects in pot experiments with mustard and barley.

Perotti (23) (24) (25) did the first systematic work in testing the fertilizing value of dicyandiamid and its salts in pots and in culture solutions. He found that solutions containing 2.5 parts per 1000 had no injurious effect, but injury was observed when the concentration reached 3 or 4 parts per 1000. In pot experiments 1 gm. in 1400 gm. of soil gave a considerable increase in yield and he concluded that the fertilizing value of calcium cyanamid depends on its polymerization into dicyandiamid in the soil. More recent work, however, does not justify this conclusion. Guanyl urea sulfate and chloride produced no injury in soil when applied at the rate of 350 to 450 pounds per acre, but in 1 per cent solutions toxicity was observed. These compounds were readily converted into ammonia in the soil. Similar views were held by Ulpiani (36). He maintained that the poisonous action of cyanamid is destroyed by the formation of dicyandiamid and urea, which are converted to ammonia and nitrate in the soil. He did not consider these intermediate products injurious in the amounts at which nitrogen is usually applied. However, de Grazia (6) reported almost no nitrate formation from dicyandiamid in soil. This fact was further demonstrated by Löhnis and Sabaschnikoff (10). They inoculated solutions of dicyandiamid with soil, but never succeeded in producing ammonia from concentrated or dilute solution.

Loew (15) (16) compared the action of dicyandiamid in sterilized and unsterilized soil, and found that on sterilized soil the yield compared favorably with that given by ammonium sulfate, while on unsterilized soil growth was seriously interfered with. This was attributed to the formation of injurious compounds from dicyandiamid through bacterial action. This conclusion is not borne out by the work of Löhnis and Moll (17) and the writers cited above, who showed that bacteria do not attack dicyandiamid. Loew observed the characteristic tip drying on both sterilized and unsterilized soil, and suggested that it was due to an excessive accumulation of dicyandiamid in that part of the plant. In 5 per cent culture solutions, severe injury was produced in two days, while in 0.05 to 0.1 per cent solutions the plants developed normally except for the dried tips.

Popp (27) (28) found no injurious effect on germination from dicyandiamid, but plants were not able to utilize it and those plants which took it up made less growth than those without nitrogenous fertilizer. Cyanamid containing 6.5 per cent of this impurity produced considerable injury. The results of Aso (1) are quite the opposite. He obtained injury from an application of 5 gm. per 10 kgm. of soil, but in smaller quantities when applied three weeks before planting no injury was apparent and the yield was almost equal to that of ammonium sulfate and cyanamid. In culture solutions 0.01 per cent dicyandiamid was a source of nitrogen for higher plants. Inouye (8) also found it a good source of nitrogen in pot experiments with barley and rape, when applied at the rate of 0.5 gm. per 8 kgm. of soil. Stutzer (33) and Stutzer and Reis (34) were unable to get an increased yield from dicyandiamid but no injury was produced if other available forms of nitrogen were present.

In the investigations of Brioux (20), Milo (21), and Söderbaum (32) dicyandiamid produced the characteristic injury to the leaf tips when applied as the sole source of nitrogen, and increasing applications resulted in decreasing yields.

Liechti (12) and Liechti and Truninger (13) conducted experiments with spoiled calcium cyanamid and obtained injury which they ascribe to the dicyandiamid contained, but this injury could be overcome by an application of readily assimilable nitrogen. Truninger (35) confirmed the results of Löhnis and others concerning the stability of the compound in soil, and even in the following year secondary ill effects on crop growth were observed in the soils which had been treated with dicyandiamid. Linter (14) also observed this stability during his investigations.

In the pot experiments of Voelcker (37) (38), dicyandiamid was not only unavailable, but depressed the yield of barley and mustard, indicating that it is somewhat injurious, although not to the extent generally alleged. He did not consider the small amounts present in ordinary nitrolin deleterious to the value of the fertilizer. However, it has not been unusual in cyanamid investigations to find samples in which 30 or 40 per cent of the nitrogen was in the form of dicyandiamid. The results of Pfeiffer and Simmermacher (29) indicate that it should not constitute more than 10 per cent of the total nitrogen. In combination with cyanamid they applied dicyandiamid to the soil in increasing amounts from 10 to 100 per cent of the total nitrogen applied. Each pot containing 15 kgm. of soil received 1.5 gm. of nitrogen. Applications above 0.16 gm. of dicyandiamid nitrogen per 15 kgm. of soil resulted in increased injury to the plants and reduction in yield. Germination was not affected by the highest application.

The results of Maze and Lemoigne (19) with culture solutions are similar to those obtained by Stutzer (33) in the soil. They grew corn in culture solutions containing 0.162 gm. of dicyandiamid per liter. When used alone it was unavailable, but in combination with nitrate of soda the plants made normal growth, thus indicating that the compound is not toxic. This conclusion is somewhat confirmed by the work of Johnson (9) (10) who found no appreciable injury from urea containing 33 per cent dicyandiamid, and concluded that the action of the compound is dependent primarily on the concentration in which it is applied.

Probably the most extensive investigation on the action of dicyandiamid is the recent work of Cowie (3). He studied the effect of small and large applications on plant growth and on biological activities in the soil. The compound itself was not decomposed in the soil, nor did it inhibit the decomposition of cyanamid and dried blood, but it did stop the nitrification process when present even in small quantities. The number of bacteria which developed on gelatin plates was in no way affected. In pot experiments the maximum application did not affect germination, but produced a marked toxicity later. Smaller quantities, 12.5–18 mgm. per kgm. of soil produced neither stimulation nor depression, although the characteristic injury to the leaf tips was present.

Mitscherlich (22), Meyer and his associates (35, 36), Hovermann and Koch (7), von Dafert and Miklauz (39) and others have observed injury from cyanamid containing relatively small amounts of dicyandiamid. Lemmermann (11) states that nitrolin should not contain more than 7 per cent dicyandiamid if it is to be acceptable as a fertilizer. His ammonification tests showed this compound and its sulfate and nitrate salts to be very stable in the soil.

While the majority of investigators have expressed an opinion that such small quantities of dicyandiamid and guanyl urea sulfate are not injurious, the results of other investigators cannot be overlooked. With the purpose of determining the effect of these small quantities the following experiment was undertaken.

THE PROBLEM

The object of this work was to determine the influence upon plant growth and microbiological activities of such quantities of dicyandiamid and guanyl urea sulfate as would be applied to the soil in a crude urea fertilizer, and to study the chemical transformation of these compounds in the soil.

GENERAL PLAN OF EXPERIMENT

Throughout the experiment, chemically pure dicyandiamid and guanyl urea sulfate were used, their analyses corresponding to the formulas given above. The investigations carried on may be divided into five parts:

1. The effect on germination.
2. The effect on plant growth in soil.
3. The effect on plant growth in culture solution.
4. The effect on microbiological activities in soil.
5. Chemical transformation of the compounds in soil.

EFFECT ON GERMINATION

Several investigators have reported no injury to germination through the action of these compounds when thoroughly mixed with the soil. In order to give a more rigid test in this experiment the compounds were distributed in the row in direct contact with the seed. Germination boxes of galvanized iron with dimensions 3 feet x 3 inches x 4 inches were sectioned off with strips of tin into 6 inch lengths, and were filled with sand. Twenty kernels of corn were placed in a row in each section directly on top of the fertilizer and covered with 1 inch of sand. Dicyandiamid and guanyl urea sulfate were applied as graduated percentages of the urea applied, ranging from 2 to 15 per cent of the total nitrogen application. The application per section was 0.4 gm. of nitrogen, based on an application of 180 pounds sodium nitrate per acre distributed along sixty rows 209 feet long. The sand was maintained at 50 and 75 per cent of its water-holding capacity. The number of seeds germinated was counted daily and observations ôn the appearance of the seedlings were made for one week. The results given in table 1 show that in no case was germination inhibited or retarded by the presence of dicyandiamid or guanyl urea sulfate, nor were the one week seedlings in any way affected.

VEGETATION STUDIES IN SOIL

This experiment was conducted in order to determine the effects of dicyandiamid and guanyl urea sulfate on plant growth, and upon the efficiency of urea containing graduated percentages of these compounds. Nine-pound portions of Collington fine sandy loam deficient in nitrogen were placed in pots and fertilized with lime, acid phosphate and muriate of potash, and a total nitrogen treatment of 0.1266 gm. per pot or the equivalent of 375 pounds of sodium nitrate per acre. Urea and the toxins were added from stock solutions and thoroughly mixed with the soil. After seeding to barley on February 24, the pots were maintained at equal and optimum moisture content by weighing and watering the individual pots daily.

Two weeks after germination each pot which had received dicyandiamid, even the smallest quantity, showed slight tip drying, but in no case did guanyl urea sulfate have this effect, even in those pots which had received this sub-

TABLE 1

Effect of dicyandiamid and guanyl urea sulfate on germination

NUM-BER	TREATMENT	NITROGEN SUPPLIED BY VARIOUS MATERIALS	WEIGHT OF MATE-RIAL ADDED	50 PER CENT SATURATED				75 PER CENT SATURATED			
				Number of seeds germinated				Number of seeds germinated			
				5 days	7 days	9 days	10 days	4 days	5 days	6 days	7 days
		per cent	*gm.*								
1	Control		0.0000	16	20	20	20	20	20	20	20
2	C. p. urea		0.2750	7	20	20	20	3	20	20	20
3	NaNO₃		0.8440	0	12	19	20	5	19	19	19
4	(NH₄)₂ SO₄		0.6330	0	5	17	18	0	5	17	17
5	NH₄ Cl		*	0	0	2	6	0	0	3	9
6	Dried blood		*	0	0	0	5	0	1	3	3
7	{ C. p. urea / Dicyandiamid	98 / 2	0.2695 / 0.0038	0	11	17	20	1	16	20	20
8	{ C. p. urea / Dicyandiamid	96 / 4	0.2640 / 0.0077	0	17	19	19	3	19	20	20
9	{ C. p. urea / Dicyandiamid	94 / 6	0.2585 / 0.0116	2	19	19	19	8	17	20	20
10	{ C. p. urea / Dicyandiamid	92 / 8	0.2530 / 0.0165	8	20	20	20	2	18	20	20
11	{ C. p. urea / Dicyandiamid	90 / 10	0.2475 / 0.0194	15	20	20	20	2	17	20	20
12	{ C. p. urea / Dicyandiamid	85 / 15	0.2338 / 0.0285	5	17	20	20	4	14	20	20
13	{ C. p. urea / G. u. sulfate	98 / 2	0.2695 / 0.0075	8	17	19	19	8	19	20	20
14	{ C. p. urea / G. u. sulfate	96 / 4	0.2640 / 0.0150	8	20	20	20	8	18	20	20
15	{ C. p. urea / G. u. sulfate	94 / 6	0.2585 / 0.0225	7	18	18	18	8	20	20	20
16	{ C. p. urea / G. u. sulfate	92 / 8	0.2530 / 0.0300	8	16	20	20	5	18	20	20
17	{ C. p. urea / G. u. sulfate	90 / 10	0.2475 / 0.0375	12	19	20	20	3	13	19	20
18	{ C. p. urea / G. u. sulfate	85 / 15	0.2338 / 0.0562	13	19	20	20	0	11	15	17

*Containing 0.1266 gm. nitrogen.

TABLE 2

Effect of Dicyandiamid and guanyl urea sulfate on plant growth and on the efficiency of urea as a fertilizer

NUMBER	TREATMENT	NITROGEN SUPPLIED BY VARIOUS MATERIALS	MATERIAL ADDED	DRY WEIGHTS AVERAGE OF DUPLICATES	INCREASE OVER CHECK
		per cent	*gm.*	*gm.*	*gm.*
1	Control		0.0000	8.42	. . . . .
2	Sodium nitrate		0.8440	19.57	11.15
3	Ammonium sulfate		0.6330	19.05	10.63
4	C. p. urea		0.2750	19.87	11.45
5	C. p. urea	99	0.2722	20.16	11.74
	Dicyandiamid	1	0.0019		
6	C. p. urea	98	0.2695	19.89	11.47
	Dicyandimid	2	0.0038		
7	C. p. urea	97	0.2667	19.43	11.01
	Dicyandiamid	3	0.0058		
8	C. p. urea	96	0.2640	20.14	11.72
	Dicyandiamid	4	0.0077		
9	C. p. urea	94	0.2585	20.22	11.80
	Dicyandiamid	6	0.0116		
10	C. u. urea	92	0.2530	21.75	13.33
	Dicyandiamid	8	0.0165		
11	C. p. urea	90	0.2475	20.01	11.59
	Dicyandiamid	10	0.0194		
12	C. p. urea	99	0.2722	19.32	10.90
	G. u. sulfate	1	0.0037		
13	C. p. urea	98	0.2695	20.69	12.27
	G. u. sulfate	2	0.0075		
14	C. p. urea	97	0.2667	20.00	11.58
	G. u. sulfate	3	0.0112		
15	C. p. urea	96	0.2640	19.63	11.21
	G. u. sulfate	4	0.0150		
16	C. p. urea	94	0.2585	21.77	13.35
	G. u. sulfate	6	0.0225		
17	C. p. urea	92	0.2530	20.45	12.03
	G. u. sulfate	8	0.0300		

TABLE 2—*Continued*

NUMBER	TREATMENT	NITROGEN SUPPLIED BY VARIOUS MATERIALS	MATERIAL ADDED	DRY WEIGHTS AVERAGE OF DUPLICATES	INCREASE OVER CHECK
		per cent	*gm.*	*gm.*	*gm.*
18	C. p. urea	90	0.2475	20.82	
	G. u. sulfate	10	0.0375		12.40
19	C. p. urea	99	0.2722	21.97	13.55
	Dicyandiamid	0.5	0.0008		
	G. u. sulfate	0.5	0.0018		
20	C. p. urea	98	0.2695	21.95	13.53
	Dicyandiamid	1	0.0019		
	G. u. sulfate	1	0.0037		
21	C. p. urea	97	0.2667	20.97	12.55
	Dicyandiamid	1.5	0.0027		
	G. u. sulfate	1.5	0.0055		
22	C. p. urea	96	0.2640	21.81	13.39
	Dicyandiamid	2	0.0038		
	G. u. sulfate	2	0.0075		
23	C. p. urea	94	0.2585	21.19	12.77
	Dicyandiamid	3	0.0058		
	G. u. sulfate	3	0.0112		
24	C. p. urea	92	0.2530	19.95	11.53
	Dicyandiamid	4	0.0077		
	G. u. sulfate	4	0.0150		
25	C. p. urea	90	0.2475	20.24	11.82
	Dicyandiamid	5	0.0095		
	G. u. sulfate	5	0.0185		
26	Dicyandiamid		0.1940	7.90	0.52
27	G. u. sulfate		0.3755	10.62	2.20

stance as the sole nitrogen treatment. Although this injury persisted in each new leaf formed, there was never any indication that growth was being retarded except in the pots which had received dicyandiamid alone. In these pots the leaves were badly burnt, and the plants were slightly smaller than the controls without any nitrogen treatment. This would indicate that its nitrogen is totally unavailable for plant metabolism, and its entrance into the plant in such large quantities causes certain disturbances which slightly retarded its growth. Hence it may be classed as a weak poison and an undesirable substance which accumulates in the plant and cannot be utilized. Those pots which received guanyl urea sulfate alone gave a slight increase over the check, tending to show that this substance becomes very slowly available as a source

of nitrogen and can by no means be considered injurious. All pots which received urea with graduated percentages of these compounds gave a good growth and were equal in yield to c.p. urea, sodium nitrate and ammonium sulfate. Urea appeared to be slightly superior to both sodium nitrate and ammonium sulfate. It must be borne in mind, when comparing these results with previous cyanamid investigations, that urea contains approximately three times as much nitrogen as does cyanamid. Consequently on an equal nitrogen basis, an application of cyanamid consisting of 10 per cent dicyandiamid contains about three times as much dicyandiamid as an equivalent application of urea containing 10 per cent of this impurity. The results of this experiment are given in table 2.

DICYANDIAMID IN CULTURE SOLUTION

In the preceding experiment, the soil moisture was maintained at 12.5 per cent of the air dry weight, so that each pot contained approximately 500 cc. of

TABLE 3

Effect of dicyandiamid on crop yield in culture solutions

	DICYANDIAMID PER LITER	DRY WEIGHT OF TOPS	DRY WEIGHT OF ROOTS	TOTAL DRY WEIGHT
	mgm.	*gm.*	*gm.*	*gm*
1	Control	7.3445	1.6927	9.0372
2	4.2	7.7727	1.7367	9.5094
3	8.4	5.8985*	1.0806*	6.9791*
4	12.6	7.2602	1.7569	9.0171
5	16.8	7.3632	1.5665	8.9297
6	25.2	. 7.0920	1.5619	8.6539
7	33.6	6.5245	1.5363	8.0609
8	42.0	7.2162	1.6349	8.8511
9	63.0	7.4077	1.7825	9.1902

*Low yield due to an injury to the roots early in the experiment.

water. Assuming this to be the soil solution, the concentration of dicyandiamid ranged from 4 to 40 mgm. per liter. In the culture solutions this concentration ranged from 4.2 to 63 mgm. per liter. These increasing amounts of dicyandiamid were superimposed on Shive's Best Solution R_5C_2, which provided ample available nitrogen. The usual cultural methods were employed. Soybeans were germinated in sphagnum moss and uniform seedlings were selected. Three seedlings placed in paraffined cork stoppers of quart jars containing the solution constituted a culture. Duplicate controls of Shive's Best Solution and duplicate cultures in each case were kept. The solutions were renewed at intervals of three and one-half days. After six weeks' growth the plants were harvested, dried at 100°C. and weighed. The results shown in table 3 do not show any appreciable difference in any of the treatments. The highest concentration, 63 parts per million, is probably as great as would be found in the soil solution of a soil which had been treated with urea containing 10 per cent dicy-

andiamid. Any toxicity should certainly be brought out in culture solution, since there is nothing to prevent its action. The results confirm those of the previous experiments, that small quantities of dicyandiamid are not injurious if other available nitrogen in present.

MICROBIOLOGICAL ACTIVITIES

Since microbiological activities are an important factor in soil fertility, it is of interest to see in what way these activities are modified by dicyandiamid and guanyl urea sulfate.

An experiment was conducted to determine the influence of these compounds on the number of bacteria and fungi in soil. Varying amounts were added to jars containing 1 kgm. of soil, and were kept at optimum moisture and temperature. The numbers of bacteria and fungi were counted at the start and at two-week intervals for six weeks. Sodium albuminate agar was used for counting bacteria and acid agar media of pH 4.2 for counting fungi. The maximum applications, 1.5 gm. dicyandiamid and 0.75 gm. guanyl urea sulfate, had no appreciable effect on the numbers of bacteria or fungi which developed on agar plates. In view of this fact one would expect no depression of biological activities in the soil as measured by ammonification of dried blood. To test this point, 200-gm. portions of the soils treated as described above were placed in tumblers and to each was added 0.5 gm. of dried blood. After the first and second week the soils were analyzed for ammonia by the magnesium oxide method and for nitrates by the phenol disulfonic acid method. The results given in table 4 are quite striking. Where no dicyandiamid was present, ammonification occurred, but the ammonia was immediately changed to nitrate, giving an increase in nitrate. The smallest application of dicyandiamid, 0.1 gm. per kilogram of soil, stopped the nitrification process and an accumulation of ammonia resulted. Guanyl urea sulfate retarded nitrification slightly but not sufficiently to allow an accumulation of ammonia. Neither substance caused any reduction in ammonia formation. Each figure in table 4 is an average of duplicates.

This marked toxic action of dicyandiamid on the nitrifying organisms is further demonstrated in the following experiment. Twenty milligrams of nitrogen as dried blood were added to 100 gm. portions of soil containing small quantities of dicyandiamid and guanyl urea sulfate, and after one month nitrate determinations were made. Nitrification was reduced from 22.6 to 3.6 per cent by the presence of 1 mgm. of dicyandiamid, while 10 mgm. of guanyl urea sulfate had no appreciable effect. The figures given in table 5 are averages of duplicate treatments.

That this toxic action persists for some time in the soil is shown in the results given in table 6. Small quantities of dicyandiamid and guanyl urea sulfate were added to 100-gm. portions of soil and the soils were kept at optimum temperature and moisture. After nine weeks, 20 mgm. of nitrogen in the form of

TABLE 4
Decomposition of dried blood in the presence of dicyandiamid and guanyl urea sulfate

TREATMENT PER KILOGRAM OF SOIL	N ADDED AS DRIED BLOOD	N PRESENT AS NH$_3$		N PRESENT AS NO$_3$	
		After 1 week	After 2 weeks	After 1 week	After 2 weeks
gm.	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*
0	0.066	0.0045	0.0047	0.0086	0.0122
Dicyandiamid					
0.1	0.066	0.0234	0.0269	0.0019	0.0018
0.5	0.066	0.0240	0.0285	0.0019	0.0019
1.0	0.066	0.0238	0.0292	0.0020	0.0020
1.5	0.066	0.0241	0.0286	0.0019	0.0019
G. u. sulfate					
0.75	0.066	0.0086	0.0089	0.0078	0.0101

TABLE 5
Nitrification of dried blood

TREATMENT PER 100 GM. SOIL	N ADDED AS DRIED BLOOD	N RECOVERED AS NO$_3$	PER CENT NITRIFIED
mgm.	*mgm.*	*mgm.*	*per cent*
0	0	0.19	
0	20	4.52	22.6
Dicyandiamid			
1	20	0.72	3.6
2	20	0.68	3.4
3	20	0.65	3.2
4	20	0.52	2.8
5	20	0.51	2.7
6	20	0.50	2.5
7	20	0.50	2.5
G. u. sulfate			
5	20	4.41	22.0
10	20	4.38	21.9

TABLE 6
Nitrification of urea

TREATMENT PER 100 GM. SOIL	N ADDED AS UREA	N RECOVERED AS NO$_3$	PER CENT NITRIFIED
mgm.	*mgm.*	*mgm.*	*per cent*
0	20	14.5	72.5
Dicyandiamid			
0.2	20	7.4	37.0
1.0	20	1.9	9.5
10.0	20	1.0	5.0
G. u. sulfate			
0.2	20	13.2	66.0
1.0	20	13.4	67.0
10.0	20	10.8	54.0

urea was added to each and incubated for a month.   Nitrate analyses at the end of this time showed marked differences.   The minimal quantity of dicyandiamid, 0.2 mgm. per 100 gm. of soil, reduced the nitrification of urea from 72.5 to 37 per cent, although nine weeks had elapsed since putting the toxin in the soil.   The reduction caused by guanyl urea sulfate is not significant. Since the toxicity of dicyandiamid on nitrification is so marked, it may be asked why nitrification of the urea was not stopped in the pot experiment and thus cause a reduction in yield.   The highest application in the pot cultures was 0.0194 gm. per pot or 0.5 mgm. per 100 gm. of soil.   This was probably sufficient to retard nitrification considerably, but not enough to cause a lack of available nitrogen at any time.   It is also possible that some of the nitrogen was utilized as ammonia, since there is abundant evidence that plants can utilize ammonia as such to good advantage.

TABLE 7

Ammonification and nitrification of dicyandiamid and guanyl urea sulfate in soil

TREATMENT PER KILO SOIL	NITROGEN EQUIVALENT	N PRESENT AS NH₃			N PRESENT AS NO₃ IN GRAMS		
		After 1 week	After 3 weeks	After 8 weeks	After 1 week	After 3 weeks	After 8 weeks
gm.	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*
0	0.0000	0.0131	0.0135	0.0143	0.0086	0.0084	0.0087
Dicyandiamid							
0.10	0.0666	0.0131	0.0193	0.0190	0.0062	0.0058	0.0060
0.50	0.3333	0.0180	0.0213	0.0214	0.0061	0.0056	0.0060
1.00	0.6666	0.0175	0.0152	0.0172	0.0055	0.0052	0.0055
1.50	0.9999	0.0180	0.0214	0.0209	0.0048	0.0056	0.0056
G. u. sulfate							
0.75	0.2500	0.0232	0.0247	0.0243	0.0075	0.0074	0.0089

STABILITY OF DICYANDIAMID AND GUANYL UREA SULFATE IN SOIL

Some investigators in the literature cited have reported that these compounds are readily broken down in the soil into ammonia and nitric acid while others have found residual ill effects from them the year following their application.   This most important point was given a test in the following way.   Dicyandiamid and guanyl urea sulfate were mixed with 1 kgm. of soil in the amounts given in table 7.   The containers were covered and were maintained at optimum moisture content.   At the stated intervals the soils were analyzed for ammonia and nitrates, so as to follow any decomposition of the compounds. The results tabulated below are in accord with the findings of Löhnis (17) and Cowie (3) and others.   After eight weeks only a trace of ammonia and nitrate was present in the soils treated with dicyandiamid, and it is probable that this ammonia was absorbed from the air in the laboratory even though precautions were taken against this.   The controls showed a higher nitrate and a lower ammonia content than those containing dicyandiamid.   This

may be explained on the assumption that in the former, the ammonia absorbed from the air was changed into nitrate, while in the latter this change was prevented by the presence of dicyandiamid. Guanyl urea sulfate showed a slight tendency to become slowly ammonified and nitrified, as was indicated in the pot experiment in which this substance gave a slight increase in yield.

SUMMARY AND CONCLUSIONS

1. Dicyandiamid and guanyl urea sulfate do not retard or inhibit germination, when applied in small quantities in direct contact with the seed.

2. Dicyandiamid is slightly toxic to plant growth when applied in large amounts as the sole source of nitrogen, but in small amounts it produces no injury except a slight tip burning, when other available nitrogen is present.

3. Guanyl urea sulfate is not toxic to plant growth in comparatively large applications, and becomes very slowly available as a source of nitrogen.

4. Minimal quantities of dicyandiamid stop the nitrification process, but do not retard ammonification. Guanyl urea sulfate retards nitrification slightly but does not affect ammonification.

5. Neither substance affects the number of bacteria and fungi in the soil.

6. Dicyandiamid is very stable in the soil. Guanyl urea sulfate is also comparatively stable, but decomposes to ammonia very slowly.

7. The fertilizing value of urea is approximately equal to that of sodium nitrate, and its value is not lessened if 10 per cent of its nitrogen is in the form of dicyandiamid or guanyl urea sulfate.

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